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16. ABSTRACT

A qualitative and quantitative assessment of the principal sources of phosphorus release to the environment was performed. Natural sources were not extensively evaluated nor were they quantified. Nonpoint sources were identified by land use; discharge data for specific land uses were obtained from the literature. Point sources were estimated on the basis of model flow diagrams and phosphorus material balances; no measured levels were utilized. The total national phosphorus emissions to air and water in 1978 were about 2.9 million metric tons. Of this amount, approximately 87.6% was attributable to nonpoint sources and 12.4% to point sources. Major nonpoint contributors are cropland runoff and pasture and rangeland runoff; for the major point sources, municipal sewage treatment was the largest single contributor. From the data developed for the national emissions, a regional assessment was performed for Florida to evaluate the difference in phosphorus sources in regions and for the nation. A cursory analysis was also performed of detergent phosphate controls in Indiana and New York. The analysis addressed surface water geography, location and nature of phosphorus water quality problems, and the impact of detergent phosphate control.

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Task I - Analysis of the Sources of Phosphorus in the Environment

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For

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Office of Toxic Substances
401 M Street, S.W.
Washington, D.C. 20460

Mr. Roman Kuchkuda
Project Officer

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PREFACE

This report presents the results of an assessment and quantification of the principal sources, both natural and anthropogenic, of phosphorus release to the environment in the United States. Also included is an analysis of certain regional eutrophication case histories in which phosphate bans were applied to detergent products.

This study was performed by Midwest Research Institute under Contract No. 68-01-3896 for the Office of Toxic Substances of the U.S. Environmental Protection Agency. The Office of Toxic Substances' project officer for this study was Mr. Roman Kuchkuda. Ms. Justine Welch of the Office of Toxic Substances served as technical advisor on this task. Principal Midwest Research Institute contributors to this study included: Mr. Charles E. Mumma (Task Leader), Senior Chemical Engineer; Ms. Kathryn Bohannon, Assistant Chemist; and Mr. Fred Hopkins, Junior Environmental Scientist. Dr. Thomas W. Lapp is the project leader for this contract, under the supervision of Dr. Edward W. Lawless, Head, Technology Assessment Section.

Midwest Research Institute expresses its appreciation to the industrial and governmental personnel who provided technical input and advice during this study.

Approved for:

MIDWEST RESEARCH INSTITUTE

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SECTION 1

INTRODUCTION AND OBJECTIVES

Phosphorus is a nutrient essential to the growth of plants and animals, as well as a raw material for a variety of commercial products. For this reason, phosphorus-derived compounds are produced and consumed in substantial quantities. In the course of these human activities, significant quantities of phosphorus-containing wastes enter the environment as air emissions, aqueous effluents, or solid residues.

In addition, a number of natural sources of phosphorus, such as runoff from undisturbed land areas, weathering of rocks, plant pollens, leaves, etc., also contribute to the environmental levels.

In most freshwater lakes and some estuarine ecosystems, the introduction of excessive quantities of phosphorus transported from any of the aforementioned sources can promote radical biological and chemical changes in the existing habitats. A few of the most easily noted changes include increased production of aquatic plants, a loss of fish species requiring water with a high oxygen content, and a general instability within the indigenous plant/animal community. The sum total of the subsequent water quality alterations is referred to as eutrophication. The ultimate result is a decline in the value of the original body of water for recreation, fisheries, or as a municipal water supply.

Although eutrophication is a complex process with several contributing factors, a reduction of phosphorus loading is often a prerequisite for the improvement of water quality. Identification and quantification of the important sources of phosphorus release to the environment are the first steps toward this important goal.

The objective of this task was to conduct an analysis on both a qualitative and quantitative basis of the principal sources (natural and anthropogenic) of phosphorus release to the environment. Phosphorus pollutants transported within a land source without reaching surface waters or discharged to subsurface waters which are not a part of the surface water inventory are not considered in this study.

Included in this report is a brief discussion of the terminology and factors related to phosphorus in the environment and its role in eutrophication.

This brief discussion will include topics such as eutrophication and the role of phosphorus, septic tanks, the effect of soil type on phosphorus movement, mechanisms of sediment release of phosphorus, chemical forms of phosphorus and their environmental fate, point and nonpoint sources, loading rates, and other factors associated with the discharge of phosphorus and its role in the environment.

The assessment of phosphorus discharges to the environment includes natural and anthropogenic, point and nonpoint sources. However, natural sources will not be discussed in as much detail as other sources, nor will any attempt be made to quantify these sources. Nonpoint anthropogenic sources are identified by land use, i.e., urban, forest, fertilized and unfertilized cropland, pastureland, etc. All sources are approximately quantified with respect to phosphorus loadings; the accuracy of these estimated loadings is unknown. No measured phosphorus loadings are reported in the quantification study. The estimated amounts of phosphorus discharged to the environment are based principally on theoretical values reported in the literature and are calculated rather than measured quantities. The estimated values have not been validated. For industrial point sources, each waste stream for all processes in each industry consuming or producing phosphorus compounds (by Standard Industrial Classification (SIC) code) is quantified with respect to phosphorus discharges, including the chemical form of phosphorus and the fate of the waste stream. Municipal discharges from sewage treatment plants are evaluated with respect to both human waste and detergent loadings. The result of this assessment will be the identification of all major point and nonpoint phosphorus discharges and the estimation of quantities associated with each anthropogenic source.

On a regional basis, the State of Florida is evaluated with respect to phosphorus discharges using the results of the national assessment. The assessment of Florida was chosen to serve as a model for other potential regional assessments. Regional assessments, which are important because of the variation which can occur in total phosphorus sources, can apply to groups of states, individual states, counties, or metropolitan areas depending upon the needs of the study. All sources will be evaluated regarding their applicability to this regional setting and the sources rank ordered. From this evaluation, the quantity of phosphorus discharge for each applicable point and nonpoint source can be estimated.

Detergent phosphorus regulations in Indiana and New York are discussed in terms of the affected sites (i.e., lakes, reservoirs, rivers, etc.) and the overall water quality impacts of these regulations.

The scope of work included the following major segments:

1. Collect the required data base and prepare a comprehensive listing of all sources of phosphorus, natural and anthropogenic, in the environment. Describe the mechanism of entry to the environment and evaluate the significance of each source.

2. Quantify each principal source identified in Part 1 on a national basis and also perform a single regional assessment as an example testing the value of Part 1 in a regional scheme.

In all emission estimates shown in this report, the term "phosphorus" refers to the total phosphorus content unless otherwise noted. All data on quantification of phosphorus sources are presented in terms of total phosphorus (i.e., kilograms (kg) of total phosphorus per metric ton (MT) of product, or metric tons of total phosphorus per year). One metric ton is equivalent to 1,000 kg or 2,205 lb.

Results of this study are presented in subsequent sections of this report, including summary and conclusions, discussion of methodology, definition and discussion of terms, identification of phosphorus sources, and quantification of principal phosphorus sources.

Conversion factors used in phosphorus terminology are presented in Appendix A. Appendix B presents typical examples of the estimating methods used in calculating the approximate phosphorus loadings for various point sources of emission.

SECTION 2

SUMMARY AND CONCLUSIONS

A summary of the results obtained in this study is presented in this section. Areas include identification and discussion of phosphorus sources, quantification and characterization of principal phosphorus sources, findings for the state regulations on detergent phosphate in Indiana and New York, and conclusions.

IDENTIFICATION OF PHOSPHORUS SOURCES

Phosphorus can be introduced into the environment from either point or nonpoint sources. The constituents of each of these sources were identified and discussed in this study.

Nonpoint Sources

Major sources of nonpoint phosphorus pollutants include runoff from cropland, pasture, forests, and rangeland, livestock feedlots, urban areas, and rural roadways. Agricultural cultivation is a major source of phosphorus water pollution. Well-managed pasture and rangeland can provide good cover to protect soil from erosion. As a result, releases of phosphorus-containing sediment from densely vegetated lands are lower than those for cropland. The term forestlands comprises a combination of recently harvested forests, logging roads, undisturbed commercial forest, and noncommercial forests. Uncontrolled livestock feedlots are sources of concentrated phosphorus-containing wastes. If improperly managed, these wastes can result in substantial pollution loads. Urban stormwater may remove phosphorus-containing wastes from both pervious and impervious surfaces and, thereby, contribute to the phosphorus pollution of receiving waters. The sources of this pollution in urban areas include soil erosion, dust and fly ash from industrial facilities, automobile leakage (e.g., engine oil and fuel residues), lawn fertilizers, organic debris from tree leaves and grass trimmings, discarded litter and pet wastes. Runoff from highways and highway rights-of-way contains significant amounts of oil, fuel residues, dust and dirt, tree leaves, and grass trimmings--all of which are sources of phosphorus.

Inadvertent nonpoint sources can also account for significant phosphorus air emissions. These sources include wind-blown soil, fertilizer application, agricultural burning, and forest fires.

Natural phosphorus discharges to surface waters occur independent of human actions. They include natural air emissions (dust, etc.), "natural runoff" (i.e., erosion and leaching from undisturbed land), decomposition products from natural communities such as algae and higher plants, and wastes from waterfowl, fish, and other fauna.

Point Sources

The major point sources of phosphorus discharge result from the mining of phosphate rock, manufacture of phosphorus-containing compounds, selected uses of these compounds, and municipal or individual sewage treatment. Discharges of phosphorus result when the rock is mined, beneficiated, and supplied to phosphate fertilizer manufacturers and producers of other chemicals.

A majority of the mined rock is utilized in the production of phosphate fertilizers. The manufacturing sites for each of the fertilizers represent a point source for phosphorus discharge whereas the release of phosphorus to the environment from the extensive use in various agricultural applications represents a nonpoint source of discharge. Relatively large quantities of phosphorus-based animal feed products are manufactured in the United States. Phosphorus losses to the atmosphere and to wastewater occur during the manufacture of these feed supplement products.

The second major use of phosphate rock is the manufacture of phosphorus-based detergents for home and commercial laundry and cleaning applications. In this instance, the manufacture and use of the detergents represent a point source discharge of phosphorus to the environment.

Phosphorus-based chemicals are used in a variety of industrial and home water treatment applications such as cooling water systems, boiler water treatment, and domestic water treatment systems. In each of these cases, the manufacture of the water treatment chemical and its application represent point sources for the discharge of phosphorus.

Additional industrial consumption of phosphorus is in the production of a wide variety of phosphorus-derived chemicals such as organophosphorus pesticides, fuel additives, pharmaceuticals, fire retardant chemicals, and food additives. The production sites for all of these chemicals represent a potential point source discharge of phosphorus. Usage of the compound may result in a point or nonpoint discharge depending upon the specific application.

Municipal sewage treatment effluent is a significant point source of phosphorus discharged to the environment. Incoming wastewater to the sewage treatment plant contains phosphorus discharges from home, commercial, and industrial applications. A portion of the phosphorus is removed by waste treatment and the remainder is discharged as treatment plant effluent.

Inadvertent point sources, such as iron and steel manufacture, cement production, refuse incineration, fuel oil combustion, and coal combustion, also contribute to phosphorus pollution.

Domestic production and apparent consumption of phosphorus in 1975 were obtained from the literature. Industrial contacts and data in the technical literature indicate that the figures are also applicable for 1978. The use patterns show that agricultural applications (including fertilizers and animal feeds) account for 83% of total phosphorus consumption. The manufacture of other phosphorus chemicals, including sodium tripolyphosphate and calcium phosphates, represents an additional 9% of total phosphorus consumption. These two groups, which account for about 92% of total consumption, are considered to include all principal industrial point sources of phosphorus. There are many miscellaneous phosphorus-based chemicals which, taken together, represent only a few percent of the total phosphorus consumption. A complete source assessment for each of these chemicals was beyond the scope of this task. The emphasis in this study was placed on the identified principal point sources and a few minor sources of phosphorus to the environment. The principal point sources investigated were:

- Agricultural products
    - Wet process phosphoric acid and phosphate fertilizers (SIC No. 2874)
    - Animal feed products (SIC No. 2048)
- Industrial products
    - Elemental phosphorus, phosphoric acid (dry process), and ferrophosphorus (SIC No. 2819)
    - Phosphorus pentoxide, phosphorus trichloride, phosphorus oxychloride, and phosphorus pentasulfide (SIC No. 2819)
    - Detergent builders (SIC No. 2841)
    - Detergent formulation (SIC No. 2841)
    - Water treatment chemicals (SIC No. 2899)
    - Food grade calcium phosphate (SIC No. 2048)
    - Direct acid (H_3PO_4) treatment of metals (no SIC number)
- Municipal sewage treatment effluent
- Inadvertent sources

The term, inadvertent sources, refers to miscellaneous manufacturing and product use activities which account for significant phosphorus losses to the environment but are generally unrelated to phosphorus-based industries or natural phosphorus sources. Examples are the manufacture of iron, steel, and cement, combustion of fuel oil and coal, wind-blown soil, agricultural burning, and forest fires.

QUANTIFICATION OF PRINCIPAL PHOSPHORUS SOURCES

Estimates of total phosphorus emissions were developed for each identified principal source (and some minor sources) on a national basis and for a selected region. The regional assessment was developed to serve as a model for possible assessments in other regions.

Data required in this study on nonpoint source phosphorus loading for runoff to surface waters were taken from the report, "National Assessment of Water Pollution from Nonpoint Sources." Air emissions from nonpoint sources were estimated using data available in the literature.

Point source emissions were estimated on the basis of model flow diagrams and phosphorus material balances developed from data in the technical literature.

Results of the analysis of phosphorus sources in the environment described in this report show that the estimated national phosphorus emissions to air and water for 1978 are on the order of 2.9 million metric tons (1 MT = 1,000 kg = 2,205 lb). Of this total, 87.6% was attributable to nonpoint sources--principally cropland runoff (~ 49%), pasture and rangeland runoff (~ 34%), and forestland runoff (3%). About 99.3% of the total nonpoint discharge comes from runoff water, with 0.7% attributable to air emissions from inadvertent sources.

Point sources account for about 12.4% of total national emissions or about 360,000 MT/year of phosphorus discharged. Municipal sewage treatment effluent represents the largest single contributor to this category (10.6%). The second and third ranking sources, in terms of emission magnitude, are water treatment chemicals (0.8%) and inadvertent sources (0.4%).

Total estimated point source air emissions account for about 55% of the 47,700 MT of phosphorus released to the atmosphere each year in the United States. (This value is included in the total national emission.) The remainder (45%) is from nonpoint air emissions. The estimated quantity of phosphorus in solid wastes is relatively small (32 MT/year).

The 10 largest 1978 national sources of phosphorus release are estimated as follows:

	Emission source category	Estimated % of national phosphorus discharge	Type of source, point (P) or nonpoint (NP)
1.	Cropland runoff	48.9	NP
2.	Pasture and rangeland runoff	33.6	NP
3.	Municipal sewage treatment effluent	10.6	P
4.	Forestland runoff	2.9	NP
5.	Total inadvertent sources	1.1	P + NP
6.	Livestock feedlots	1.0	NP
7.	Phosphorus-based water treatment chemicals (usage)	0.8	P
8.	Urban runoff	0.6	NP
9.	Phosphate rock mining and beneficiation	0.2	P
10.	Production of phosphorus and chemicals	0.2	P
	Total	99.9	

Regional assessments are important because of the variation in total phosphorus sources which can occur from one region to another. These regional assessments can be for groups of states, individual states, counties, or metropolitan areas, depending upon the needs of the study. The methodology shown for the assessment of Florida can serve as a model for other regional assessments.

For the selected regional study (Florida), the estimated total phosphorus emission is about 34,000 MT/year or about 1.2% of national emissions.

The total nonpoint emissions in Florida represent about 57% (~ 19,500 MT) of the total estimated phosphorus emission for the state. In this category, runoff water discharges account for about 56% of total emissions, with about 1% attributable to inadvertent nonpoint sources.

The estimated total emission from point sources in Florida amounts to about 14,600 MT of phosphorus or approximately 43% of the entire statewide discharge. The largest point source discharges are municipal sewage effluent (21%), phosphate rock mining and beneficiation (10.7%), production of animal feed (~ 5%), and production of phosphate fertilizer and intermediate chemicals (4.2%). Inadvertent point discharges account for about 1.2% of the total for the state.

The estimated 10 largest environmental phosphorus pollution sources in Florida in terms of total phosphorus discharge are:

Emission source category	Type of source	Estimated % of Florida phosphorus discharge	Estimated % of national discharge*
1. Pasture and rangeland runoff	NP	37.9	33.6
2. Municipal sewage treatment effluent	P	21.0	10.6
3. Cropland runoff	NP	13.7	48.9
4. Phosphate rock mining beneficiation	P	10.7	0.2
5. Animal feed production (feed grade calcium phosphates and defluorinated phosphate rock)	P	4.8	1.0
6. Phosphate fertilizer and intermediate chemical production	P	4.2	0.2
7. Forestland runoff	NP	2.4	2.9
8. Inadvertent sources (total)	P + NP	2.3	1.1
9. Urban runoff	NP	1.5	0.6
10. Use of phosphorus-based water treatment chemicals	NP + P	0.7	0.8
Total		99.2	99.9

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* Percent for emission source category.

The distribution of phosphorus discharges in Florida thus seems to be quite different from that at the national level. For example, in the national assessment the ratio of total nonpoint to point emissions is about 7 to 1. In contrast, for Florida the estimated nonpoint to point source emission ratio is about 1.3 to 1. The cropland runoff emissions are 48.9% of the total in the national assessment and only 13.7% of the total for Florida.

A contrast also exists in the distribution of point source discharges at the national and Florida levels. On a national basis, municipal sewage effluent accounts for about 10.6% of the total phosphorus discharge; in Florida the sewage effluent accounts for 21% of total phosphorus discharge. Phosphate rock mining and processing and fertilizer and animal feed production in Florida represent a much higher proportion of total phosphorus discharge than in the case of the national assessment (about 20% in Florida versus 0.4% for the nation). These differences point out the difficulty in applying national phosphorus emission figures to regions or localities.

In some regional settings, phosphorus sources that are minor on a national scale may take on major significance, e.g., discharge of municipal sewage plant effluents into an urban lake. Thus, for regional studies of phosphorus sources, the high potential for these special pollution problems should be recognized. Cognizance should also be given to the special demand and usage of small volume phosphorus-containing chemicals in certain regions of the United States. For example, the concentrated use of the stable aryl phosphates as fire retardant hydraulic fluids in metropolitan areas may lead to significant contamination of receiving waters because of leakage or disposal.

ANALYSIS OF DETERGENT PHOSPHATE LEGISLATION IN INDIANA AND NEW YORK

A cursory analysis was conducted of detergent phosphate controls in the states of Indiana and New York. This study addressed the surface water geography, the location and nature of phosphorus water quality problems, and the impact of the detergent phosphate control.

The principal findings of this study were:

1. Sewage treatment effluents are the major point source of phosphorus loading in these states.

2. A significant portion of the aquatic habitat in Indiana and New York contained phosphorus at levels (> 25 μg/liter in lakes and reservoirs, > 50 μg/liter in rivers emptying into reservoirs, and > 100 μg/liter in free flowing rivers) which indicated eutrophic conditions prior to the 1973 legislation.

3. Phosphorus loading on Indiana rivers decreased by about 20% during the first 2 years of the state's detergent phosphate ban.

4. Despite the improvement noted, major segments of the Wabash, White, and Grand Calumet rivers in Indiana remained eutrophic (> 100 μg/liter of total phosphorus) 2 years after the detergent ban was initiated. As noted previously in Item 1, sewage treatment effluents are major point sources of phosphorus loading. The flushing action provided by high water flows and the rarity of anaerobic conditions in rivers tends to minimize the possibility that sediment release might have sustained high phosphorus levels. However, the present data for rivers in Indiana are inconclusive with respect to the cause of the current phosphorus levels. For lakes in Indiana, the shortage of data precludes any conclusions to be drawn.

5. The available data are insufficient to permit an analysis of the phosphorus loading reduction in New York as a result of the statewide detergent phosphate ban. Data on file with the New York State Environmental Conservation

Department, which records effluent parameters of the National Pollution Discharge Elimination System (NPDES) permittees, have not been sufficiently compiled to allow the determination of any changes in phosphorus loading. Also, MRI is not aware of any additional studies to duplicate the lake sampling of the National Eutrophication Survey. Such an effort would quantify any improvements in lake/reservoir water quality which may have occurred since the enactment of the phosphate legislation.

CONCLUSIONS

1. On a national basis, nonpoint sources (principally cropland or pasture and rangeland) apparently account for about 88% of all phosphorus emissions discharged to the environment. The effective control of these nonpoint sources would drastically reduce phosphorus loadings to the nation's surface waters. A critical factor in the limitation of nonpoint phosphorus discharge to the environment is the improved management of agricultural and other developed land to minimize phosphorus pollution caused by runoff.

2. A comparison of regional (Florida) and national emissions of phosphorus demonstrates that national control of phosphorus is likely to be inappropriate in some cases. Therefore, phosphorus emission control schemes which address regional activities would (if implemented) probably be more effective than national control methods. Localized and regional problems should be assessed individually.

3. Achievement of improved municipal sewage treatment for phosphorus removal appears to be an important priority leading to water quality improvement, with respect to those regional settings where these effluents are a major source of phosphorus loading to lakes.

4. Certain apparently minor sources of phosphorus losses on a national basis may take on major significance in individual regional settings (e.g., specific metropolitan areas) because of unusually heavy concentrations of producers and/or consumers of phosphorus-based chemicals. An example case is pollution of an urban lake by phosphorus contained in industrial discharges. Care must be exercised in assessing phosphorus emissions on a local or regional level to avoid overlooking these problems.

5. Atmospheric pollutants (i.e., particulate matter) containing phosphorus can be an important source of phosphorus loading in surface waters. It has been reported that this source contributed one-fifth to one-third of the total phosphorus entering Lake Michigan in 1974.

SECTION 3

DISCUSSION OF METHODOLOGY

A discussion of the methodology used for the data acquisition and quantification of phosphorus sources is provided in this section.

DATA ACQUISITION AND ANALYSIS

Initially, the U.S. Environmental Protection Agency (EPA) provided a series of technical articles related to this task. Information contained in these articles concerned the breakdown of total phosphorus loadings to surface waters. All summaries and abstracts in these articles and documents were reviewed and, as appropriate, utilized in this study.

Literature Search Activities

A number of data sources were investigated as a means for supplementing the above data base. Published data pertaining to industrial sources of phosphorus release were obtained from the following technical documents:

- Encyclopedia of Chemical Technology.[1/]
- Chemical and Process Technology Encyclopedia.[2/]
- Chemical Process Industries.[3/]
- Industrial Chemicals.[4/]
- Directory of Chemical Producers.[5/]
- Chemical Economics Handbook (Phosphorus Chemicals)[6/] (1975, 1976, 1977).
- Annual reports and workshop proceedings of the International Joint Commission.[7-9/]

A search was made of computerized data in the files (DIALOG) of the National Technical Information Service (NTIS) using keyword descriptions. Subject areas covered in this search included phosphorus release to the environment by air emissions, wastewater effluent, solid wastes, and septic tank systems. A computerized search of Dissertation Abstracts was employed to identify current research findings on nonpoint phosphorus loading from agricultural sources. This search surveyed all Ph.D. theses entering the data file during the last 10 years for selected keywords. A limited amount of useful information was identified by these searches.

Telephone and Letter Inquiries

Numerous telephone and letter contacts were made with governmental agencies (state and national), trade organizations, and industry sources to identify and collect available data relating to the qualification and quantification of point sources (both municipal and industrial) of phosphorus release to surface waters. Information was obtained on potential methods of data retrieval, technical articles of interest, waste management practices, and probable data gaps. With few exceptions, most of the information acquired was of a general nature and very few quantitative data were obtained. The contacts were generally reluctant to divulge any detailed information on discharged process wastes.

Telephone inquiries concerning phosphorus loading from agricultural sources were made to various departments of the agricultural colleges of Iowa State University, the University of Nebraska, Kansas State University, the University of Wisconsin, and the Potash and Phosphorus Institute. Little useful data were obtained from these sources.

Computer-Based Data Retrieval Systems

The feasibility of acquiring useful phosphorus pollution data from the EPA STORET system under the National Pollution Discharge Elimination System (NPDES) program was searched for industrial plants discharging effluent into navigable waterways. A trial search of this system, through the cooperation of the EPA Region VII office (Kansas City), was made for the years 1975 and 1976. MRI assisted in the selection of keywords for this search. The results showed that very little point source data were available. The NPDES program is a source of effluent data on phosphorus for those permits which specify it. However, since few industrial permits specify this material, individual discharges are difficult to trace even for those industries discharging phosphorus to a municipal treatment plant that regularly reports phosphorus. It was concluded that this system could not provide the required point source data for this study.

Another potential alternative data source is the discharge monitoring and permit compliance information compiled by state pollution control agencies. Telephone inquiries relating to the use of these data sources were made to the states of Florida, Louisiana, Texas, Kansas, Missouri, Arkansas, Iowa, Michigan, and New Jersey. Four of these states (Arkansas, Iowa, Missouri, and Kansas) had no data or very little information on phosphorus sources. The remaining states indicated that visits to their offices would be necessary for data review and compilation. It was concluded that it would not be feasible to collect information by this procedure.

EPA Data on Effluent Limitation Guidelines

A review was made of the available EPA development documents on effluent limitation guidelines for new source performance standards for applicable point source discharges of industries of interest to this program. New source performance standards for applicable industries were also reviewed. The subject areas reviewed in these documents were:

* Minerals for the Chemical and Fertilizer Industries,[10]

* Basic Fertilizer Chemicals,[11]

* Phosphorus Derived Chemicals,[12] and Draft Supplement,[13]

* Other Nonfertilizer Phosphate Chemicals,[14]

* Soap and Detergent,[15] and

* Animal Feed, Breakfast Cereal, and Wheat Starch.[16]

QUANTIFICATION OF PHOSPHORUS SOURCES

The quantification consisted basically of a study of two major subcategories of phosphorus emissions: nonpoint sources and point sources of discharge to the environment. The nonpoint sources are those which result in diffuse discharges, while point sources are those which discharge phosphorus from discrete, measurable points.

The quantification studies were essentially limited to the principal sources identified in the early phases of this study.

Nonpoint Sources

A recent draft report, "National Assessment of Water Pollution From Nonpoint Sources,"[17] discusses the results of a study by MRI which quantitatively assessed various nonpoint pollutant loads (including phosphorus) for the United States. A published companion report, "Loading Functions for Assessment of Water Pollution From Nonpoint Sources,"[18] discusses the development and use of loading functions for determining nonpoint loads (including phosphorus). The phosphorus-loading functions cover runoff discharges from the following sources: (a) cropland, (b) pasture and rangeland, (c) forestland, (d) livestock feedlots, (e) urban areas, and (f) rural roadways. Information taken from these two reports served as the data base for quantifying the nonpoint phosphorus loading in this study.

Emissions for sources (a) through (c) were calculated by an approach in which the estimated quantities of phosphorus contained in eroded sediments were summed for each source. The basic formula used was the Universal Loss Equation.[19] The basic emission estimating method used for livestock feedlots consisted of a method to estimate feedlot runoff from precipitation characteristics of a region and data on phosphorus concentrations in runoff and feedlot sizes. For urban runoff estimates, the basic information source was several studies on the rates of deposition of phosphorus-containing pollutants in representative urban areas and other data on the rates of delivery of phosphorus in runoff. A more detailed discussion of the methodology for estimating nonpoint phosphorus loading is presented in Section 6.

There are a number of other current technical reports dealing with nonpoint phosphorus loading and assessments of phosphorus discharge. A brief discussion of some noteworthy reports, which were reviewed and referenced in this study, follows.

A recent investigation by the Corvallis Environmental Research Laboratory,[20] "Nonpoint Source--Stream Nutrient Level Relationships: A Nationwide Study," includes data on nonpoint phosphorus loads. Stream nutrient runoff and watershed characteristics for 923 nonpoint source watersheds across the nation were analyzed.

Some of the most comprehensive, localized activity on phosphorus assessment has occurred in connection with the Canada-U.S. Great Lakes Water Quality Agreement. Annual reports from the International Joint Commission's Great Lakes Water Quality Board,[7] Reference Group on Great Lakes Pollution From Land Use Activities,[8] and the Research Advisory Board[9] contain considerable information on nonpoint phosphorus discharge in the Great Lakes area.

In 1976, J. H. Gakstatter and associates reported on the results of a survey by the EPA, "Lake Eutrophication: Results From the National Eutrophication Survey."[21]

The U.S. Geological Survey has reported recently on the "Development of Phosphate Resources in Southeastern Idaho."[22] This includes a final environmental impact statement.

Point Sources

Effluents from municipal sewage treatment plants are a point source of phosphorus discharge. Estimates of these discharges were developed on the basis of annual per capita phosphorus loads (including inputs from laundry detergents, automatic dishwashers, garbage disposals, and personal sewage) and on estimated phosphorus inputs from commercial establishments and industry. The 1976 Needs Survey[23] was used to obtain information on the population served by primary, secondary, and tertiary sewage treatment facilities (excluding the nonsewered population). A detailed discussion of the estimating methods used for quantifying phosphorus loads in treated sewage effluent is presented in Section 6.

To the extent possible, industrial discharges were quantified on the basis of models developed for production or use processes. Representative process flow diagrams include phosphorus balances and available data on unit emission rates for phosphorus. Supporting data used to develop these model process flow sheets and accompanying descriptions were taken largely from EPA effluent limitations guidelines,[10-16] a report on the inventory of sources and emissions of phosphorus,[24] and industrial contacts.

These process diagrams show, wherever possible, the phosphorus balance, losses, and chemical forms present in each waste stream for each product of interest. In addition, the process diagrams indicate the fate of the waste streams (atmosphere, water, landfill, etc.).

For each industrial process diagram, unit phosphorus emission factors, based on the production rate of 1 MT of product, were developed. These emission factors applied to (a) discharges of total phosphorus in process wastewater effluent per metric ton of product and (b) discharges of total phosphorus in air emissions per metric ton of product.

The application of these unit emission factors requires the use of production or consumption rate data for products of interest. Since the published rate data were not current, the production/consumption rates were adjusted using growth trend data obtained from technical publications or from industry contacts.

For the national assessment, the total annual production/consumption rates for the products of interest (e.g., elemental phosphorus production) were multiplied by the emission factors derived from the appropriate process flow diagram.

In addition, reported data on national inadvertent point sources[25] were updated by using 1978 production/consumption rate trend factors.

Appendix A lists conversion factors used in phosphorus terminology. Appendix B presents descriptions of typical methodology used to calculate the estimated total phosphorus emission from industrial point sources.

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SECTION 4

DEFINITION AND DISCUSSION OF TERMS

INTRODUCTION

This section provides a discussion of technical terms associated with phosphorus, its transport in the environment, and implications for eutrophication. Specific chemical forms of phosphorus and associated parameters are discussed. A distinction is made between point and nonpoint sources with major point sources in the phosphorus industry being categorized by SIC codes. Other discussions focus on the availability of phosphorus as a nutrient and the chemistry of phosphorus movement in soils and sediments. Because of the importance of sewage-related phosphorus, septic tanks and municipal sewage treatment systems are discussed.

EUTROPHICATION

Eutrophication is the process by which waters become enriched with nutrients. The primary manifestation of eutrophication is the acceleration of algal biomass production. This increase in the growth of aquatic plants and the resulting ecosystem alterations, collectively labeled "eutrophication," most frequently takes place in lakes and reservoirs, but may also be observed in backwaters and sloughs of rivers and in portions of estuaries.[1-4]

Eutrophication may occur at a slow rate as nutrients derived from an undisturbed watershed fertilize progressively larger crops of algae over a period of thousands of years. Alternately, the trophic state of a body of water may remain the same for hundreds of years and not become "eutrophic"--as long as nutrient input does not exceed losses--or the nutrient loading can actually decrease with time in rare cases.[3] However, the enrichment process may also take place rapidly due to nutrient contributions from human, urban, agricultural, or industrial activities (cultural eutrophication).[1-4]

The key nutrient in the eutrophication of most fresh waters is phosphorus in the form of orthophosphate. Phosphorus is one of about 21 nutrients that may be required for algal growth. According to Liebig's Law of the Minimum, any of the 21 essential nutrients will become growth-limiting if present in the shortest supply relative to the amount needed. Phosphorus is the limiting nutrient in most lakes.[1-5]

Exceptions to this last statement include waters that exhibit a naturally occurring deficiency of some other nutrient, or waters that receive phosphorus in uncommonly high amounts. The latter circumstance is sometimes observed in eutrophic lakes. In these cases, nitrogen frequently becomes the limiting nutrient--not because nitrogen is in short supply, but because phosphorus and other nutrients are present in excess.[3/]

Both carbon and nitrogen are required in larger quantities than phosphorus for plant growth and reproduction (ratio of atoms--$C:N:P \simeq 106:16:1$),[2/] but they are both readily available to aquatic ecosystems via the solubility of atmospheric CO_2 and N_2. In addition, blue-green algae are capable of fixing atmospheric nitrogen. Since phosphorus has no such atmospheric reservoir, it is usually the limiting nutrient in lakes undisturbed by man; this is also the reason why phosphorus is generally considered to be the most easily controlled nutrient.[6/]

When phosphorus is the limiting nutrient in a lake, eutrophication may be controlled--in many instances--by restricting the inflow of this nutrient. However, in lakes which have reached advanced stages of eutrophication prior to the implementation of phosphorus control measures, recycling of orthophosphate from hypolimnetic* water during seasonal overturns (usually spring and autumn) may sustain problem algal growth. Because of this self-fertilization process, the duration of the waiting period between nutrient loading reductions and measurable improvements is hard to predict. This time lag has been hypothesized to approximate three times the phosphorus residence time of the given body of water.[2/]

In different aquatic ecosystems, eutrophic conditions must be characterized separately. Lakes and storage reservoirs (which are, in effect, man-made lakes) are similar in their response to nutrient loading. Major parameters used to indicate eutrophic conditions in lakes and reservoirs include: total phosphorus > 25 µg/liter, chlorophyll > 10 µg/liter, Secchi disc visibility < 2.0 m, and $< 10\%$ hypolimnetic dissolved oxygen saturation.[7/]

This terminology is not normally applied to undammed rivers, but slow-moving portions of rivers that mimic ponds or small lakes can be affected by nutrient enrichment. Geologically and biologically, the life cycle of a river is different from that of a lake. The flushing action of high water conditions and the ability to meander preclude the death of a river by sedimentation. Natural flowing waters contain plant and animal life which contrasts sharply with that present in lakes. Whereas it is not uncommon for eutrophic lakes to support vast populations of both attached and free-floating algae, the river environment usually does not allow this degree of problem growth. The motion of stream water is well suited to some species of attached algae but discourages many others and practically eliminates macrophytes.*[8,9] However, rivers below major impoundments contain a plankton that reflects that of the impoundment.

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* The hypolimnetic water (or hypolimnion) is the deep zone in a thermally stratified lake.

Many rivers carry large sediment loads, particularly during spring thaws or rainy seasons. Light penetration is greatly limited by the amount of suspended sediment, and the potential for plant growth is reduced. In addition, the erratic changes in water level which characterize rivers allow only the most hardy species of aufwuchs** to survive. As a result, a river habitat may provide only a narrow zone near the water surface and along the shoreline suitable for the growth of algae and macrophytes, and the productivity of this shoreline zone may be further reduced by water level fluctuation.[8]

Recent water quality criteria recommendations by the EPA have taken into account the inherent differences between lake and river habitat response to phosphorus loading. Because rivers are less susceptible than lakes to eutrophication and its associated problems, higher levels of dissolved phosphorus are considered tolerable in rivers. The level of total phosphorus (as phosphorus) not to be exceeded in rivers is 100 μg/liter. At any point where a river enters a reservoir, the recommended limit is lowered to 50 μg/liter. Within lake or reservoir basins, the figure is 25 μg/liter.[10]

Estuaries also must be considered separately in a discussion of eutrophication. Permissible phosphorus concentrations determined for lake, reservoir, or river habitats are not applicable. In phosphorus-limited estuaries (many estuaries are not phosphorus limited[1,11]), benthic oxygen depletion has been postulated to reach critical levels as a result of total phosphorus concentrations higher than ~ 55 μg/liter during the summer or ~ 80 μg/liter during the winter in estuaries located in northern temperate climates.[12]

The hazard of nutrient enrichment in an estuary is due largely to the high retention of nutrients characteristic of estuaries. The mechanism of this nutrient retention may be explained as follows. As the less dense surface layer of fresh water flows seaward, it drops much of its nutrient-rich sediment. An opposite flow of more dense deeper sea water returns these sediments back into the estuary. Tidal fluctuations and river currents further complicate this general description of estuary circulation in different locales; however, the common phenomenon seen is a nutrient-rich zone where biological productivity is higher than either the adjacent ocean or fresh water.[9]

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* Macrophytes are aquatic plants that are large enough to be observed with the unaided eye (in contrast to the many species of microscopic phytoplankton).

** Aufwuchs consists of generally small plants or animals attached to any submerged substrate.

When nutrients provided by fresh water entering an estuary become excessive, the results are similar to those seen in eutrophic lakes. The standing crop of algae increases, decomposition of the resulting biomass accelerates, benthic* organisms experience oxygen shortages, and the ecosystem is generally disrupted. Because estuaries provide a necessary habitat for many shellfish and fish fry, as well as a pathway for the spawning runs of some species of fish; these conditions have serious repercussions for commercial fisheries.[9]

General symptoms of eutrophication in all bodies of water include: (a) a decrease in phytoplankton diversity; (b) an increase in phytoplankton production; (c) changes in species composition of aquatic organisms, such as a shift to blue-green algae and rough fish species; (d) a decrease in the transparency of water; (e) the depression of oxygen concentration in the hypolimnia of lakes during periods of stratification; (f) the buildup of total phosphorus and nitrogen concentrations; and (g) an increase in the growth of dense floating algal mats.[13,14]

Adverse consequences of eutrophication include:[13,14]

* Interference with recreational and aesthetic uses of surface waters.

* Odor, taste, and filtration problems in domestic water supplies caused by algal blooms.

* Increased cost for water treatment (domestic and industrial water supplies).

* Problems with agricultural uses of water (obstructions in irrigation canals, etc.).

* Toxicity of some blue-green algae to wild and domestic animals.

* Elimination of valuable game and commercial fish species and associated industries.

* Cost for the cleanup of eutrophic waters.

* A decline of property values in water-based communities.

PHOSPHORUS ANALYSES

Types of Phosphorus

Phosphorus may be reported in 12 different analytical forms in studies of eutrophication problems.[15] These forms are noted in Table 4-1.

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* Benthic means indigenous to the bottom.

TABLE 4-1. FORMS OF PHOSPHORUS REPORTED IN ANALYTICAL MEASUREMENTS

Form No.	Phosphorus material
1	Total phosphorus
2	Total dissolved phosphorus
3	Phosphorus [in suspended solids][a] (insoluble)
4	Phosphorus [in particulates (mud)][a]
5	Total hydrolyzable phosphorus (polyphosphorus + some organic phosphorus)
6	Dissolved hydrolyzable phosphorus
7	Insoluble hydrolyzable phosphorus
8	Total organic phosphorus (phosphorus incorporated into animal and plant detritus
9	Dissolved organic phosphorus (natural organic waste, fecal material, etc.)
10	Insoluble organic phosphorus (natural organic waste, fecal material, etc.)
11	Dissolved orthophosphate (PO_4^{-3}, $H_2PO_4^{-1}$, HPO_4^{-2}, and ions of polyphosphoric acids)
12	Insoluble orthophosphate (apatite, and inorganic complexes)

[a] pg. 249: ". . . [methods] may not be applicable to sediment-type samples, . . . but . . . data . . . not available at this time to warrant such usage when [P contents] are required."

Source: Reference 15.

"Total phosphorus" includes all analytically detectable forms of phosphorus. Dissolved or soluble phosphorus includes organic and inorganic phosphates that are available as plant nutrients. Dissolved phosphorus has the most direct impact on eutrophication.[2] Phosphorus may also be adsorbed onto insoluble suspended solids. Phosphorus in particulates (mud) are those solids found in lake or river bottom sediments. These particulates are not immediately available as plant nutrients; however, they do represent an inventory of stored phosphorus which can be released by acidic chemical reactions and aerobic biological activity. Hydrolyzable phosphorus includes compounds that can be chemically decomposed by breaking a bond and adding the elements of water. Hydrolysis of phosphorus compounds can have a significant effect on eutrophication. For example, hydrolysis of polyphosphate compounds (e.g., from laundry detergents) can result in the soluble orthophosphate forms that are readily available as a plant nutrient. The soluble orthophosphate form is sometimes referred to by analytical chemists and by researchers as soluble reactive phosphorus.

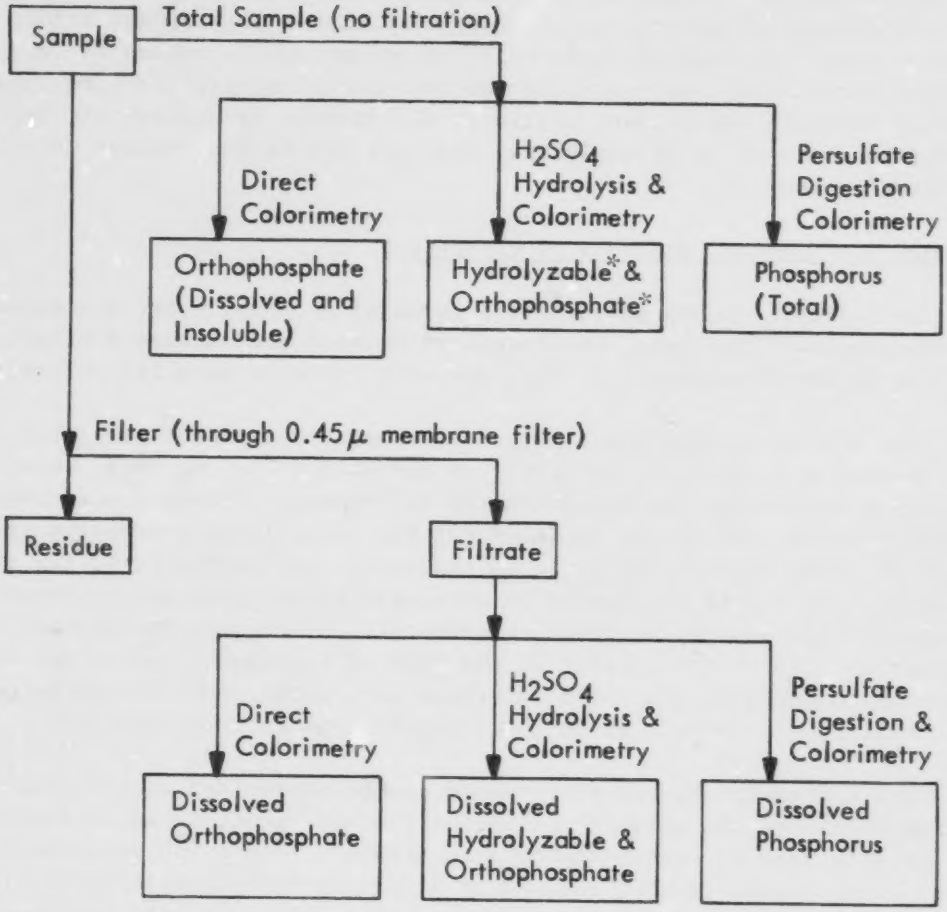
Methods for Chemical Analysis of Phosphorus

Analytical methods covering all forms of phosphorus are discussed in an EPA document.[15] The basic analytical techniques are discussed briefly herein, and the reader is referred to this document for more detailed information.

The two basic analytical methods for total phosphorus are: (a) the single reagent method, which is usable in the 0.01 to 0.5 mg total phosphorus per liter range; and (b) the automatic colorimetric ascorbic acid reduction method which is applicable in the 0.001 to 1.0 mg total phosphorus per liter range.[15] Both methods are based on reactions that are specific for the orthophosphate ion and on the use of colorimetric techniques. Only orthophosphate phosphorus is measured by these colorimetric techniques. The methods are very similar and differ principally in the type of equipment used in the analytical measurements. As indicated in Figure 4-1, determinations can be made on the total sample as well as on the filtrate from filtered samples.

The automatic colorimetric method can be summarized as follows.[15] Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of orthophosphorus to form an antimony-phospho-molybdate complex. This complex is then reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the orthophosphate concentration. In these tests, only orthophosphate forms a blue color. Polyphosphates and some organic phosphorus compounds may be converted to the orthophosphate form by sulfuric acid hydrolysis. Organic phosphorus compounds are converted to the orthophosphate form by persulfate digestion.

Total phosphorus (P, all phosphorus present in the sample, regardless of form) is measured by the persulfate digestion procedure. The total orthophosphate content $[(PO_4)^{-3}]$ is measured by the direct colorimetric procedure and is designated P-ortho.[9]


Sample
Total Sample (no filtration)
Direct Colorimetry
H_2SO_4 Hydrolysis & Colorimetry
Persulfate Digestion Colorimetry
Orthophosphate (Dissolved and Insoluble)
Hydrolyzable* & Orthophosphate*
Phosphorus (Total)
Filter (through 0.45 μ membrane filter)
Residue
Filtrate
Direct Colorimetry
H_2SO_4 Hydrolysis & Colorimetry
Persulfate Digestion & Colorimetry
Dissolved Orthophosphate
Dissolved Hydrolyzable & Orthophosphate
Dissolved Phosphorus

* These forms are not synonymous.

Source: Reference 15.

Figure 4-1. Analytical scheme for differentiation of phosphorus forms.

Total hydrolyzable phosphorus (P-hydro) is measured by sulfuric acid hydrolysis and a colorimetry procedure with a correction provided by subtraction of predetermined orthophosphate values. The hydrolyzable phosphorus includes polyphosphorus [$(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$, etc.] plus some organic phosphorus.[9]

The content of total organic phosphorus (P-org) in samples is determined by the persulfate digestion procedure after correction by subtraction of hydrolyzable phosphorus and orthophosphate values.

Total dissolved phosphorus (P-D) is defined as all of the phosphorus present in the filtrate of a sample passed through a filter of 0.45 μpore size.[15] This form of phosphorus is measured by the persulfate digestion procedure. Dissolved orthophosphate phosphorus (P-D, ortho) is measured by the direct colorimetry procedure. Dissolved hydrolyzable phosphorus (P-D, hydro) is determined by the sulfuric acid hydrolysis procedure allowing for subtraction of predetermined dissolved orthophosphate values. The content of dissolved organic phosphorus (P-D, org) is measured by the persulfate digestion procedure with the subtraction of predetermined values of dissolved hydrolyzable phosphorus and orthophosphate.

When sufficient amounts of insoluble forms of phosphorus are present in samples to warrant consideration, the forms which may be calculated are:[9]

Insoluble phosphorus	(P-I) = (P)-(P-D)
Insoluble hydrolyzable phosphorus	(P-I, hydro) = (P, hydro)-(P-D, hydro)
Insoluble organic phosphorus	(P-I, org) = (P, org)-(P-D, org)

CHEMICAL REACTIONS AND TRANSPORT OF PHOSPHORUS

Phosphorus in Natural Waters

The forms of phosphorus in natural waters are indicated in Table 4-2 and discussed in the following paragraphs.

Inorganic Phosphates--

These compounds may include the ions of orthophosphoric acids ($H_2PO_4^-$, HPO_4^{-2}, PO_4^{-3}) and polyphosphoric acids $(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$, etc.[16] The orthophosphate ions generally comprise 40 to 50% of the total phosphorus present in natural stream water regardless of adjacent land usage.[16]

Inorganic phosphates may be present in either a dissolved form or as part of suspended matter (e.g., particles of apatite [$Ca_{10}(PO_4)_6F_2$] or inorganic

TABLE 4-2. FORMS OF PHOSPHORUS PRESENT IN SURFACE AND WASTEWATERS

Dissolved phosphorus		Suspended phosphorus		
Orthophosphate $[(PO_4)^{-3}]$	As organic colloids and/or combined with an adsorptive colloid	As mineral particles (e.g., apatite) and/or adsorbed on inorganic complexes such as $Fe(OH)_3$	Organisms	Adsorbed on detritus and/or present in organic compounds
←Total phosphorus in filtrate→				
←Total phosphorus content of unfiltered water→				

Source: Reference 4.

complexes). Dissolved inorganic orthophosphates are the forms of phosphorus most easily used as a nutrient by algae and other photosynthesizing plants.[16]

Because inorganic orthophosphate is recognized as the principal form of phosphorus utilized in plant nutrition, much of the literature addressing the role of phosphorus in eutrophication concentrates on the relative abundance of orthophosphate. However, current research indicates that inorganic phosphorus compounds often comprise less than 10% of the total phosphorus present in aquatic ecosystems.[17] Soluble inorganic phosphorus is only a transient component of lake or river water. Living cells quickly utilize such compounds because of their critical need for phosphorus.[18]

Organic Phosphorus Compounds--

Naturally produced organic phosphorus is derived from intracellular organic matter as well as extracellular orthophosphate.

They include nucleoproteins, phospholipids, teichoic acids (a major component of bacterial cell walls and membranes), aminophosphoric acids, and sugar phosphates or their decomposition products.[16]

Organic phosphorus in natural waters is present in five major storage sites: living and dead suspended particulate matter, filterable organic compounds, rooted and encrusted bottom plants, free-living animals, and bottom sediments.[4] The significance of the large quantity of phosphorus represented by these five reservoirs is increased by rapid recycling from one site to another or from one organism to another. The movement of phosphorus from dying cells into the surrounding water and the subsequent uptake by nearby living cells has been studied with the use of radiophosphorus (P^{32}). Bacteria have demonstrated the ability to uptake, utilize, and excrete phosphorus within minutes.[19]

Photosynthesis is a process of photophosphorylation in which inorganic phosphate and ADP (adenosine diphosphate) combine chemically in sunlit cells to yield ATP (adenosine triphosphate). This synthesis is the primary source of energy in autotrophic cells. The energy is released when needed by reversing the reaction ($\text{ATP} \longrightarrow \text{ADP} + \text{inorganic P} + \text{energy}$). Similar biochemical processes utilizing organic phosphates are responsible for energy storage and use in heterotrophic cells, as well.

Aside from the importance of phosphorus in energy transformation within cells, phosphorus is also essential in the production of many cellular constituents, including phosphoproteins and nucleic acids.[18]

Phosphorus in Wastewaters

The principal forms of phosphorus in municipal wastewater are: orthophosphates $(PO_4)^{-3}$, polyphosphates or condensed phosphates $[(P_2O_7)^{-4}, (P_3O_{10})^{-5}$, etc.], and organic phosphorus compounds (fecal material, garbage disposal waste, etc.).[20,21]

Generally, soluble orthophosphates are available as nutrients to all forms of life, while phosphorus in other oxidation states is not immediately available.[20,21] Condensed phosphates, such as pyrophosphates and tripolyphosphates, will hydrolyze in natural waters or during wastewater treatment to the usable orthophosphate form. No data specifying hydrolysis time were found in the technical literature.

Phosphorus in Sediments and Phosphorus Cycling Within Lakes

Phosphorus in surface water sediments can result from decomposition of organic matter, the physical buildup of phosphorus-containing plant debris (e.g., dead algae and also terrestrial vegetation), chemical precipitation, and ion exchange with iron, aluminum, and calcium. In acidic lake sediments, inorganic phosphorus is largely combined with iron and aluminum, while in alkaline sediments, calcium phosphate predominates.

Phosphorus exchange between bottom sediment and the surrounding water is critical to the maintenance of a lake ecosystem. In the absence of human activity, phosphorus is typically the limiting nutrient in a lake.[18] As a result, all phosphorus entering a lake is of great value, and life forms present in lakes have developed mechanisms to make the best use of the available phosphate. Natural recycling processes reuse phosphorus in a series of algae crops. The following example will serve to illustrate the foregoing discussion.

When dead leaves are windborne or waterborne into a lake, they accumulate on the lake bottom. In aerobic shallows they become a feedstock for invertebrates and bacteria. Likewise, if anaerobic conditions exist (as might be the case at the bottom of the hypolimnion of a eutrophic lake), the leaves become the fuel for the metabolic activity of anaerobic bacteria. In either case, the phosphorus present in the original leaf tissue is incorporated into the microorganisms, which populate the lake bottom. These cells, in turn, are a food source for detritivores.*

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* Detritivores are organisms that inhabit the debris at the surface of the bottom sediment under aerobic conditions.

Twice a year in second order dimictic* lakes located in temperate climates (with the exception of meromictic lakes**), the nutrients that are dissolved or present as suspended solids in hypolimnetic water are distributed throughout the lake by overturns. These events are physical phenomena that result from the seasonal temperature (density) changes of the lake water.[22]

During the summer months, the water beneath a lake's metalimnion, the boundary zone between warmer surface waters and the cooler waters of the hypolimnion, tends to establish a temperature close to that of the local groundwater (10 to 16°C or 50 to 60°F) with a slight heating effect possible from bacterial metabolism of sediment. Thermal stratification prevents oxygen of atmospheric origin from entering the hypolimnion. Hypolimnetic nutrients are, similarly, unable to enter the epilimnion (the warmer, surface water). During the fall, decreasing atmospheric temperatures cool the lake water above the metalimnion to a temperature equal to or below that of the hypolimnion. The density difference between shallow and deep water is reversed. Subsequently, the metalimnion temporarily ceases to exist, and the lake water literally "overturns." The nutrient-rich hypolimnetic water comes to the surface to fertilize algal growth, and the highly oxygenated, cold surface water sinks into the depths to provide a fresh oxygen supply for benthic organisms. In lakes that have a winter ice cover, a similar overturn event occurs during the spring thaw.[3]

As a result of these overturns, the phosphorus present in the original leaf tissue is now available to algae growing in the epilimnion.*** As the vegetation thrives, dead plant debris slowly settles to the lake bottom where the phosphorus is again utilized by saprophytic**** organisms and becomes part of the semiliquid ooze which lines the lake basin. Overturns recycle the phosphorus until it precipitates into a stable inorganic complex or some other form too heavy for overturn transport, or until it is washed out of the lake basin by an outlet stream.

In the warmest regions of the United States (Florida, southern Texas, and southern California), stratified lakes may not establish the uniform temperatures from surface to bottom necessary for an overturn, even once a year. Nutrient transport from hypolimnetic water and sediment is, thereby, severely restricted.

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* A second order dimictic lake is a lake of moderate depth (~ 10 to 30 m maximum depth) in which two overturns (spring and fall) occur annually.

** Meromictic lakes are chemically stratified due to the intrusion of saline waters or salts liberated from sediments. This stratification is permanent, and only the epilimnion circulates.[9]

*** The epilimnion is the upper layer in a thermally stratified lake.

**** Saprophytic organisms are those bacteria and fungi that utilize decaying organic matter as a substrate for growth.

The preceding description of lake overturn is applicable to many of the larger lakes and reservoirs in the continental United States; however, numerous smaller third order lakes and ponds are too shallow to stratify ($\leq$ 10 m maximum depth).[3] The most shallow of these lakes ($\lessapprox$ 5 m maximum depth[23]) are very vulnerable to eutrophication, even in the absence of man-made ecosystem disruptions. (European limnologists first used the term "eutrophic," to describe lakes of this type.[3])

Sunlight is available to a much larger percentage of the water in a shallow lake than would be the case in a deep stratified lake. The lack of depth encourages the growth of rooted plants as well as free-floating ones. Dead algae support a large population of microorganisms at the lake bottom. Water circulation caused by wind and simple diffusion continually reintroduces nutrients to the (trophogenic)* zone near the water's surface. It is not uncommon for the rate of biomass decomposition in such a lake to consume so much oxygen that fish kills occur.[23]

Regardless of the area covered or the depth of a lake, when the level of total phosphorus present in the lakewater exceeds the $\sim$ 25 μg/liter suggested for eutrophic conditions, there is an increase in plant production. Observations of the contrasting algae/macrophyte populations occurring in eutrophic and oligotrophic** lakes demonstrate this heightened production, as do the results of laboratory bioassay procedures designed to quantify the ability of lakewater to produce algal biomass.[24]

Another result of high phosphorus levels in lake water is an increase in the amount of phosphorus contained in or adsorbed on algal cells. Algae are able to stockpile phosphorus when it is abundant. This ability is known as luxury uptake.[25] Two consequences of the formation of this living reservoir of phosphorus in eutrophic waters are: (a) significant quantities of phosphorus (much of which is likely to be orthophosphate[25]) are made available to growing algae when mature plants die and decay, and (b) significant quantities of phosphorus are deposited in the sediments as a constituent of plant debris and, thus, are available for recycling by way of biological, physical, and physical-chemical processes.

When the activities of human society (i.e., municipal waste disposal, agriculture, industrial waste disposal) enrich the phosphorus content of lake water, the natural mechanisms designed to conserve and recycle phosphorus continue to function. Over a period of a few years, the sediment layer may accumulate a high amount of phosphate and biomass that could require thousands of years for deposition under natural runoff conditions. The lake basin fills with sediment at an accelerated rate. Anoxic conditions may develop beneath the metalimnion because of oxygen depletion due to decaying organic matter. As a result, the diversity of benthic species (but not necessarily biomass) is drastically reduced.

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* Trophogenic zone is the zone of net increase in biomass.

** Oligotrophic lakes are nutrient-poor and support only meager algae populations.

The biological processes involved in the sedimentary phosphorus cycle command much attention in a discussion of eutrophic growth potential; however, purely chemical changes also occur.[26] Phosphorus can be released from lake sediment by desorption mechanisms. The reduction of ferric to ferrous ions is thought to be an important triggering mechanism in the desorption of phosphorus from iron-containing sediment. When hypolimnetic dissolved oxygen is depleted by oxidation of organic matter, there is a decline in the pH and the oxidation-reduction potential at the sediment surface. A mechanism which limits molecular and/or ionic diffusion between sediment and water under aerobic conditions is broken down. This mechanism is thought to involve a ferric oxide barrier which is eliminated by the formation of soluble ferrous phosphate under the circumstances just mentioned. Subsequently, orthophosphate is able to diffuse from the bottom mud into the hypolimnetic water.[12]

SOURCES OF PHOSPHORUS

Definitions and brief discussions of point sources and nonpoint sources of phosphorus discharge to the environment are presented in the following paragraphs.

Point Sources

These sources deliver phosphorus to surface waters or the atmosphere in discrete, measurable streams.[22] Examples include the wastewater discharge pipes at municipal sewage treatment plants or chemical processing plants, and the vent pipes and chimneys on factory buildings used to discharge waste gases to the atmosphere.

Nonpoint Sources

A nonpoint source is a pollution-generating activity which results in diffuse discharges of phosphorus-containing materials.[22] The nature of nonpoint sources is very diverse, as the following examples will illustrate. They usually originate from either the lithosphere or the biosphere, and the actual emission may enter surface waters, the atmosphere, or be deposited on the land. Emission may be made from the atmosphere, from surface waters, or from land.

Examples of water-based nonpoint emissions include sewage and garbage disposal from commercial ships or recreational boats on inland lakes or waterways, as well as ocean dumping of sewage, garbage, and other wastes.

Examples of land-based nonpoint emissions are:

- Runoff from major land use areas such as croplands, pastures, rangelands, forests, livestock feedlots, urban districts, and rural roadways.
- Leaching from improperly managed or constructed landfills and trash dumps.
- Septic tank systems.
- Emissions caused by applications of phosphorus-based fertilizers and biocides to lawns, gardens, farms, and managed forest areas.
- Forest fires.
- Burning of agricultural wastes.
- Deciduous tree leaves.

Rainfall and other forms of precipitation (e.g., snow or dry fallout such as settled dust) contaminated with phosphorus are examples of pollution discharged from the atmosphere to either surface waters or land areas.

Phosphorus Load

The phosphorus load from any given source entering surface waters is the weight of total phosphorus discharged to the receiving waters per unit of time (e.g., mass of total phosphorus expressed as kilograms phosphorus per unit of time).22/ The load may result from various sources, such as watershed runoff or point effluent discharges from municipal sewage treatment plants or industries. Part of the loading may be due to air pollutants (e.g., particulates containing phosphorus with adsorbed phosphorus which settle into surface waters).

The background phosphorus load is that portion of the total phosphorus load which is attributable to natural effects such as runoff from land apparently undisturbed by man's activities (e.g., runoff from native forestland, leaching of exposed phosphate rocks which are part of an unmined ore deposit, etc.).22/

Phosphorus Burden

Phosphorus burden is the in-stream total phosphorus concentration determined by water quality measurements. Some of the phosphorus load discharged to streams can be converted by physical or chemical changes to forms which deposit on the stream bottom and thereby decrease the phosphorus concentration in the water. Background burden is the phosphorus concentration determined under circumstances which approximate a condition undisturbed by man.22/

Standard Industrial Classification (SIC) Codes

The SIC categorizes industries over the entire field of economic activities. It is revised periodically to reflect the changing industrial composition of the economy.[27]

The SIC was developed for use in classifying establishments by type of activity; to facilitate collection, tabulation, presentation, and analysis of data relating to establishments; and to promote uniformity and comparability in the presentation of statistical data collected by agencies of the U.S. government, state agencies, trade associations, and private research organizations.[27]

A list of phosphorus-related SIC codes is shown in Table 4-3. All of these industries either have phosphorus waste streams or discharge phosphorus inadvertently by process material leaks and spills during manufacturing operations. The industries in these SIC codes are sources of phosphorus discharge to the environment.

Other industries which also have significant phosphorus discharges to the environment or to municipal treatment facilities include the many segments of the food and fiber industries. When fluids and cells from once-living tissues enter wastewaters, organic phosphorus compounds will be present. Phosphorus levels in production wastewaters are increased further, whenever sanitation or production efficiency requires the extensive use of detergents.

SOILS AND PHOSPHORUS MOVEMENT

Soils contain a mixture of inorganic particles with various compositions and sizes (particles less than 2 μ have colloidal properties) and enmeshed organic matter with a wide range of molecular weights.[16] A portion of the interparticle voids in undisturbed soil is occupied by water, living plant roots, and macro- and microorganisms, and the remainder of the volume is the gaseous soil atmosphere.

The inorganic colloidal (clay mineral) portion of the soil is comprised mainly of aluminum silicate polymers.[16] Silica is leached from the clay minerals, leaving behind $Al(OH)_2^+$ groups that are active in specific adsorption of polybasic anions, including all phosphate compounds.[16] When phosphate fertilizers and polyphosphates used in industry and agriculture are introduced into a soil, these compounds hydrolyze rapidly to orthophosphate by the activity of soil microorganisms and chemical hydrolysis.[16] No information was found in the literature concerning the time frame in which this hydrolysis occurs.

TABLE 4-3. PRODUCTS UTILIZING PHOSPHATE ROCK-DERIVED PHOSPHORUS ARRANGED BY SIC CODE[a,b]

Industry No.	Description
	Chemical and Fertilizer Mineral Mining
1475	Phosphate rock
1479	Other fertilizers not elsewhere classified (i.e., guano)
	Grain Mill Products
2045	Blended and prepared flour (phosphated flour)
2047, 2048	Food products for pets and livestock
	Beverages
2086	Bottled and canned soft drinks and carbonated waters (H_3PO_4 use)
	Industrial Inorganic Chemicals
2819	Industrial inorganic chemicals not elsewhere classified: phosphates (except defluorinated and ammoniated phosphorus, phosphorus oxychloride, etc.)
	Drugs
2834	Pharmaceutical preparations
	Soaps, Detergents, and Cleaning Preparations
2841, 2842	Soaps, other detergents, and specialty cleaning products
	Industrial Organic Chemicals
2865	Cyclic crudes, cyclic intermediates, dyes, and organic pigment lakes and toners
2869	Industrial organic chemicals: triphenyl phosphate, phosphoric acid esters
	Agricultural Chemicals
2874	Phosphatic fertilizers, phosphoric acid

(continued)

TABLE 4-3. (continued)

Industry No.	Description
2875	Fertilizers, mixing only
2879	Pesticides and agricultural chemicals not otherwise classified

[a] Adapted from Reference 27.

[b] This table includes the primary products in which mined P enters the U.S. market.

Soil phosphorus has been classified into the following general categories: calcium phosphate, aluminum- and iron-phosphate, and organic phosphorus compounds. The quantity of phosphorus in the organic portion of the soil is reported to range from 15 to 80% of the total phosphorus.[16] Residues of plants and living and dead macro- and microorganisms comprise the organic portion of the total phosphorus content.

One of the most significant characteristics of phosphorus in the soil is its general immobility.[29,30,31] Essentially all phosphorus applied as fertilzzer is converted to water insoluble forms within a few hours. When the soil is undisturbed, the phosphorus moves little over a period of years. However, in cultivated soils, the phosphorus is redistributed through the plow depth (approximately 15 cm). Except for well-drained soil areas on which applications of large amounts of both water and fertilizer are used, essentially none of the phosphorus moves downward by water percolation to the groundwater table.[30]

One reason for the immobility of phosphorus is the element's strong adsorption to finely divided soil particles (e.g., clay minerals, iron and aluminum oxides, and some organic materials). The maximum concentration of phosphorus in soil solution extracts is reported to be about 0.1 ppm, even for soils which have been heavily fertilized.[29] About 40 to 50% of this total phosphorus in soil solution is present as orthophosphate.[16]

In addition, phosphorus applied to soil can become immobilized because of its reaction with cations. In acidic soils, the formation of insoluble iron and aluminum phosphate reduces the availability of phosphorus as a fertilizer.[22] In alkaline soils, orthophosphate may react with calcium carbonate to produce relatively insoluble hydroxyapatite according to the reaction:

$$6HPO_4^{2-} + 10CaCO_3 + 4H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 10HCO_3^- + 2OH^-$$

Phosphorus adsorbed on soils can migrate overland with soil solids to water systems.[29] Erosion of topsoil, carrying phosphates directly to rivers and lakes, is more important in water fertilization than the relatively small amounts of phosphorus which may be transported via percolation to subsoil waters.[28] Overland transport (erosion) is the principal nonpoint mechanism of phosphorus loss from land sources. The sources of phosphorus in the soil that are subject to transport by erosion include: (a) naturally occurring phosphorus; (b) applied commercial fertilizers and manures; and (c) plant residues.[22]

The phosphorus originally bound in the soil generally remains immobilized and is not subject to a significant amount of transport by solubilization.[28,29,30] Under certain circumstances, however, such as highly acidic soil conditions (e.g., caused by bacterial activity, high sulfur content soils, or excessive fertilizer applications), solubilization and transport of phosphorus can occur. In general, phosphorus remains bound in the soil and is transported principally by soil erosion (i.e., sediment in runoff).[28]

Much of the phosphorus applied to land is retained in the soil as unavailable mineral phosphorus or transported through erosion to receiving waters. Soil management practices to reduce erosion (e.g., reduction of fall plowing, minimum overall tillage, terracing, strip cropping, etc.) could decrease phosphorus losses from runoff and reduce the subsequent impact on water quality.[29,30,31]

Leaching from septic tank tile fields can contribute nutrients (e.g., phosphorus and nitrogen) to groundwaters with the most significant transport resulting from tile fields constructed in coarse sand, gravel, or soil types which are low in clay and silt content.[18] Sands and gravels do not have a significant adsorptive capacity for phosphorus and, therefore, these materials do not bind phosphorus in the soil. The key to retaining phosphorus within an aquifer system is the presence of clay minerals, organic matter, iron oxide, aluminum oxide, and limestone. Because of the high adsorptive capacity of most soils for phosphorus, only small concentrations of phosphorus are usually found in waters entering streams from groundwater aquifers.[29]

PHOSPHORUS REMOVAL

Septic Tanks

Septic tanks are the most numerous type of wastewater treatment and disposal system serving an estimated 50 million Americans in homes and other small dwelling units.[32] The popularity of such devices is of course related to the needs of remote sewage treatment but also because of the simplicity and accepted efficiency of these units. The septic tank is an acceptable method of treatment for individual disposal systems (e.g., residences, schools, camps, institutions, etc.) where municipal waste treatment is not available.[18]

A septic tank system consists of a detention tank and an adjoining lateral field. The wastewater enters the detention tank where settleable solids are accumulated with concomitant biological decomposition. Grease and other floatables can also be captured so that only the nonsettleable liquid portion of the wastewater leaves the tank and enters the lateral field. Periodically the accumulated solids should be removed by pumping for ultimate disposal in larger treatment plants.

The lateral field consists of trenches, piping, and gravel whereby the septic tank effluent is distributed into the soil for ultimate disposal. This fraction of the wastewater ultimately ends up in the groundwater by seepage or in the atmosphere via evaporation. However, the constituents themselves are subject to numerous interactions with the soil and can accumulate in this medium.

The soil phase of the septic tank system is the most crucial because a failure can cause the incoming wastewater to backup and/or to seep to the surface of the ground. This occurs because of inadequate soil conditions, weather extremes, interfering vegetation and groundwater, or wastewater overloads.

The soil microorganisms are the main characters in the treatment processes occurring within the lateral field. They convert biodegradable organic matter to new cells. Solids carried over from the septic tank are accumulated and decomposed on the underdrain surface. Numerous biological transformations can occur depending upon the particular environment that exists within the soil system, e.g., the aerobic metabolism of the wastewater will create a slime layer on the trench wall which will reduce the infiltration of the wastewater into the surrounding soil. This reduction will in turn cause the liquid to be retained longer in the soil so that other desirable chemical reactions can occur which will reduce the movement of the components into the groundwater. An overgrowth of this layer, caused by wastewater overloads or inadequate resting time, would plug the soil so that flooding and seepage occurs without proper treatment of the wastewater contaminants.

In a normal septic tank system, a dynamic phosphorus balance is established in the soil which comprises the effluent drain field. Some of the phosphorus originally adsorbed on soil particles is converted by soil microorganisms to highly stable cellular protein forms (i.e., humus). This microbial action releases phosphorus from adsorption sites and helps to maintain an adequate adsorption capacity for phosphorus in the septic tank drain field. Plant roots also take up some of this phosphorus if the field is not too deep.

Although most septic tank systems are in continuous use, there are those which serve on a discontinuous basis, especially those at recreational areas such as camps, retreats, etc. Concern is expressed for the performance of such installations because of the die-off (due to starvation) of the microorganisms responsible for the stabilization of the contaminants in the wastewater. This is not a valid concern because a significant portion of domestic sewage is the microorganisms. Besides these mirobes, the soil organisms will remain dormant until the right environmental conditions reappear. There are adequate seed microorganisms to initiate the biological processes necessary for the treatment of such intermittent discharges. In fact, as with all soil systems, there needs to be a resting period so that the microbes can recover from system overloads.

There are some conceivable natural and anthropogenic causes of phosphorus desorption and migration in soils. In some isolated instances, septic tanks may be situated in soils having a relatively high sulfur content (e.g., the presence of iron pyrites in areas near coal mines). Soils containing sufficient amounts of pyrite minerals can generate acidic soil solutions which are capable of solubilizing and transporting phosphorus. Also, it is probable that acidic solutions generated by excessive applications of nitrogen fertilizer (e.g., ammonium nitrate) or phosphate fertilizer near septic tanks could cause desorption and migration of phosphorus in the soil.

In general, the components contained in septic tank effluents are retained in the soil system while the treated liquid passes on to the environment. However, it should be realized that the capacity of any system can be exceeded and soils are no exception. As mentioned above, excesses and poor designs can result in incomplete treatment and pollution of the environment.

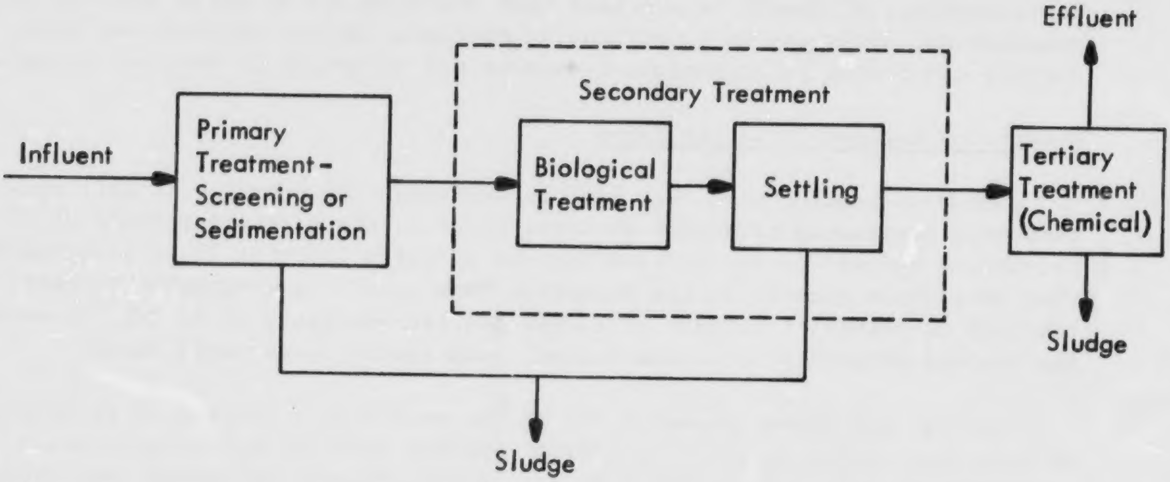
Phosphorus Removal in Septic Tanks

Numerous studies have been made to determine the behavior of soil systems as a wastewater treatment process. However, the particular study of phosphorus removal in septic tank systems is quite limited. It is recognized that phosphorus removal in the detention tank itself is comparable to that achieved in primary treatment at larger facilities, i.e., 10 to 20%. However, the removal accomplished in the lateral soil system is not well known.

Sawhney and Starr presented one of the most recent reviews of phosphorus removal in a septic tank drainfield.[32/] Spatial measurements of phosphorus were made around a trench over a 2-year period. Results indicated that phosphorus removal was quite effective (90 to 99+%) and occurred in the first 30 cm of the soil. Furthermore, it was speculated that soils with a deep water table should have adequate capacity to remove phosphorus for a number of years. However, the authors cautioned that shallow soils with high or perched tables would likely permit undesirably large additions of phosphorus to the groundwater. A similar conclusion was reached by Viraraghaven and Warnock who measured phosphorus removals of only 25 to 50%.[33/]

Sewage Treatment Processes

The effect of increasing pollution load on the environment has resulted in the development of more efficient means to treat man's wastes. For domestic sewage, the evolution of process development has moved from primary to tertiary treatment as illustrated in Figure 4-2. The particular level of treatment used by a community will depend upon many factors but most municipalities are providing or will provide secondary treatment according to P.L. 92-500. Some cities are or will provide advanced or tertiary treatment because of their unique wastewater characteristics and limited water resources for effluent disposal.


Effluent
Secondary Treatment
Influent
Primary Treatment - Screening or Sedimentation
Biological Treatment
Settling
Tertiary Treatment (Chemical)
Sludge
Sludge

Source: Reference 34.

Figure 4-2. Simplified flow diagram of municipal sewage treatment.

Primary Treatment--

This treatment can be considered as solids treatment. Early efforts to control municipal pollution involved the separation of solids from domestic sewage with their subsequent treatment. This usually involved screening, sedimentation, and anaerobic digestion.[34] The inorganic solids were eventually disposed of on the land and the organic solids were stabilized or rendered less obnoxious in a biological process of anaerobic digestion. Residue from this process was also returned to the land.

Of course other treatment methods have evolved to accomplish primary treatment but they all deal with reducing the environmental effects of sewage solids.

Secondary Treatment--

Solids treatment alone was not adequate to keep pace with the changing environmental situation, so secondary treatment was added to accomplish a more complete degree of pollution control. Basically, secondary treatment involves the removal of residual biodegradable organics from a primary process. These compounds are colloidal and soluble in nature and thus require another means for their removal (other than mechanical or physical). The most common method of removal is by biological treatment using the various types of trickling filter or activated sludge processes.[34]

The trickling filter process involves the use of a support media (rock, wood, plastic, etc.) for microorganisms which are responsible for the removal of the biodegradable contaminants left in the primary treatment effluent. The process is considered facultative, i.e., it operates with and without oxygen. The wastewater is trickled over the media coated with microbes and after treatment is sent to a sedimentation tank where accumulated biosolids are removed.

The activated sludge process is an aerobic or oxygen dependent treatment scheme where primary effluent contaminants are converted to biosolids in a liquid environment called an aeration tank. It does not use support media, intermittent or trickling application, or partially aerated liquid as does the trickling filter. Usually a higher degree of treatment is accomplished in the activated sludge process. This is due to the improved process control and aerobic environment.

The sedimentation tank following the aeration tank is used to separate the biosolids from the treated wastewater. These solids can be reused in the aeration tank to facilitate the treatment efficiency. It is important that this part of the activated sludge process perform satisfactorily or biosolids can be lost to the effluent with reduced overall treatment efficiency.

Tertiary Treatment--

Any treatment over and above secondary is referred to as tertiary and it can take many forms depending upon the environmental situation. The most common treatment concerns include nutrient (phosphorus and nitrogen), refractory organic, pathogen, residue solids, or trace metal removals. Treatment methods vary according to the particular components but include such processes as chemical precipitation, stripping, breakpoint chlorination, carbon adsorption, ion exchange, etc.[34] Thus far, it can be concluded that such advanced treatment schemes are not commonplace but are used where special environmental concerns exist, e.g., phosphorus removal where eutrophication is a problem.

A relative idea of approximately how much third-degree treatment (primary, secondary, and tertiary for phosphorus removal only) costs when compared to second-degree treatment (primary plus secondary) was obtained by a review of technical literature.[35] The capital investment and operating costs for the three-degree system are estimated to be about 34% and 67% higher, respectively.

Phosphorus Removal Processes--

Phosphorus removal is usually considered necessary when it is identified as the causative agent for eutrophication. Various treatment methods exist for its removal but the most common (hence economical) is by chemical addition. This is the subject of a revised manual on phosphorus removal by EPA.[36]

The basic mechanisms of phosphorus removal by chemical addition involves precipitation and/or colloidal destabilization. When the solubility products of phosphorus salts are exceeded, then chemical precipitation will occur. Hence, chemicals are selected which will form these salts with phosphorus so that the phosphorus in the wastewater will become insoluble and can be removed by sedimentation and/or filtration. Quite often the phosphorus has been complexed into colloidal forms by combination with other contaminants in the wastewater. Such particulate forms of phosphorus can be effectively removed by colloidal destabilization using chemicals.

Colloidal destabilization consists of coagulation which involves the interaction of the treatment chemical with the colloids creating an unstable suspension and flocculation which involves the interaction of the chemically destabilized colloids to form a settleable suspension. Mineral chemicals like alum, aluminate, and iron salts are used as coagulants to accomplish phosphorus removal. Lime is also used as a coagulant and a chemical precipitant.

The 1976 EPA manual on phosphorus removal reviews the treatment alternatives for phosphorus removal from domestic wastewaters using the above mentioned chemicals. Six basic methods are described with supportive data from actual field and pilot studies. These methods include chemical addition at various points along the conventional treatment train where a phosphorus suspenion can be removed by sedimentation and/or filtration. This involves removal in the primary, secondary, or tertiary sedimentation basins.36/

Typical removal efficiencies are summarized later in Table 6-14 but it should be recognized that such removals are site specific, i.e., one must investigate and determine what leveals of removals can be accomplished with a particular wastewater-chemical combination. However, in general, deliberate attempts to remove phosphorus by chemical treatment is significantly better than the unintentional phosphorus removal accomplished in conventional treatment for solids and biodegradable organic removals.

Phosphorus Removal from Municipal Wastewater by Chemical Precipitation Methods--

Demonstration tests conducted in Canada have shown that is is feasible to chemically treat wastewater for phosphorus removal during primary or secondary treatment operations without using the relatively expensive tertiary treatment methods described earlier.

Full-scale tests in municipal wastewater treatment plants in Ontario, Canada, during the period of 1971 to 1975, have demonstrated that removal of phosphorus from wastewater effluents by chemical precipitation is a feasible and cost effective method for reducing phosphorus discharge to water bodies.37/ Precipitation of phosphorus compounds by the use of lime, iron, or aluminum compounds have been investigated in both primary and secondary treatment plants. In contrast to tertiary treatment by coagulation to remove several pollutants, the primary purpose of these precipitation methods is to remove phosphorus.

Basic statistics for the Canadian study program on chemical phosphorus removal are shown in Table 4-4. When iron (as ferric chloride) or alum was used as the chemical precipitant, the average dose requirements and the chemical costs were considerably higher for raw wastewater treatment than for addition to mixed liquor. The lowest average chemical cost for addition to raw wastewater applies for the process which uses lime as a treatment chemical.37/

Treatment processes using lime as a phosphorus precipitant--The calcium ion reacts with phosphate ion in the presence of hydroxyl ion to form hydroxyapatite.36/ The approximate equation for the reaction can be written as follows, assuming that the phosphate is present as HPO_4^{2-}:

$$3\ HPO_4^{2-} + 5\ Ca^{2+} + 4\ OH^- \longrightarrow Ca_5(OH)(PO_4)_3 + 3\ H_2O$$

The process (high lime) described below for treatment of raw wastewater, with lime added in the primary treatment unit, can consistently produce phosphorus levels below 1 mg/liter when flocculant aids and filtrations are used.36/

TABLE 4-4. BASIC STATISTICS FROM THE CANADA-ONTARIO FULL-SCALE TREATABILITY STUDY PROGRAM--TO ACHIEVE AN EFFLUENT PHOSPHORUS REQUIREMENT OF 1 MG/LITER

		Addition to raw wastewater primary treatment plant			Addition to mixed liquor secondary treatment plant		
Chemical	Total No. of plants	No. of plants	Avg dose (mg/ℓ)	Avg cost[a] ($/million gallons)	No. of plants	Avg dose (mg/ℓ)	Avg cost[a] ($/million gallons)
Iron	22	7	16.0[b]	26.9	15	9.2	15.0
Alum	20	5	10.3[b]	33.5	15	7.2	21.7
Lime	3	3	118[c]	25.5	-	-	-

Source: Reference 37.

a/ Chemical cost only (December 1974, from consultants).

b/ Dosages as milligrams per liter Fe/Al.

c/ Dosages as milligrams per liter Ca.

High lime treatment of domestic wastewaters is just one of the numerous treatment alternatives for phosphorus removal. Excess lime addition in the primary portion of a sewage treatment will significantly increase phosphorus removal over conventional primary treatment; also, it will allow increased removals over low-lime treatment in the primary. This is accomplished by adding lime before the primary clarifier in order to raise the wastewater pH to 11.0 or 11.5. The phosphorus will be precipitated as hydroxyapatite, leaving an effluent with less than 1 mg/liter/phosphorus. In addition, the water will be softened, viruses deactivated, and heavy metals removed. Finally, the residual phosphorus will be further reduced in the secondary portion of the treatment plant by biological uptake.36/

The addition of lime before the primary clarifier requires either chemical feeding equipment to produce a lime slurry or direct addition to the wastewater. Either way, the lime must be uniformly mixed with the wastewater. After lime dosage to the proper pH, the wastewater can be gently mixed in a preaeration basin or flocculation tank to facilitate the production of a chemical precipitate (flox) which is subsequently removed in the primary clarifier; however, this is not always a necessity.

The volume of sludge produced in the primary clarifier is increased markedly over conventional treatment. This increased volume is due to the phosphorus, hardness, and heavy metal precipitates. Also, improved removal of suspended solids will occur. This has the effect of reducing these loadings on the secondary biological treatment process and increasing them on the anaerobic digestion or other solids processes. Research has shown that this increased sludge loading is not detrimental to anaerobic digestion, but in fact can improve the dewaterability of the sludge in the final treatment steps of sand beds, centrifuges, or vacuum filters.

Another possibility of lime sludge treatment is the recovery of the lime by recalcination. EPA suggests that plants treating more than 10 million gallons per day (mgd) may find this method of chemical reuse economical.

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SECTION 5

IDENTIFICATION OF PHOSPHORUS SOURCES

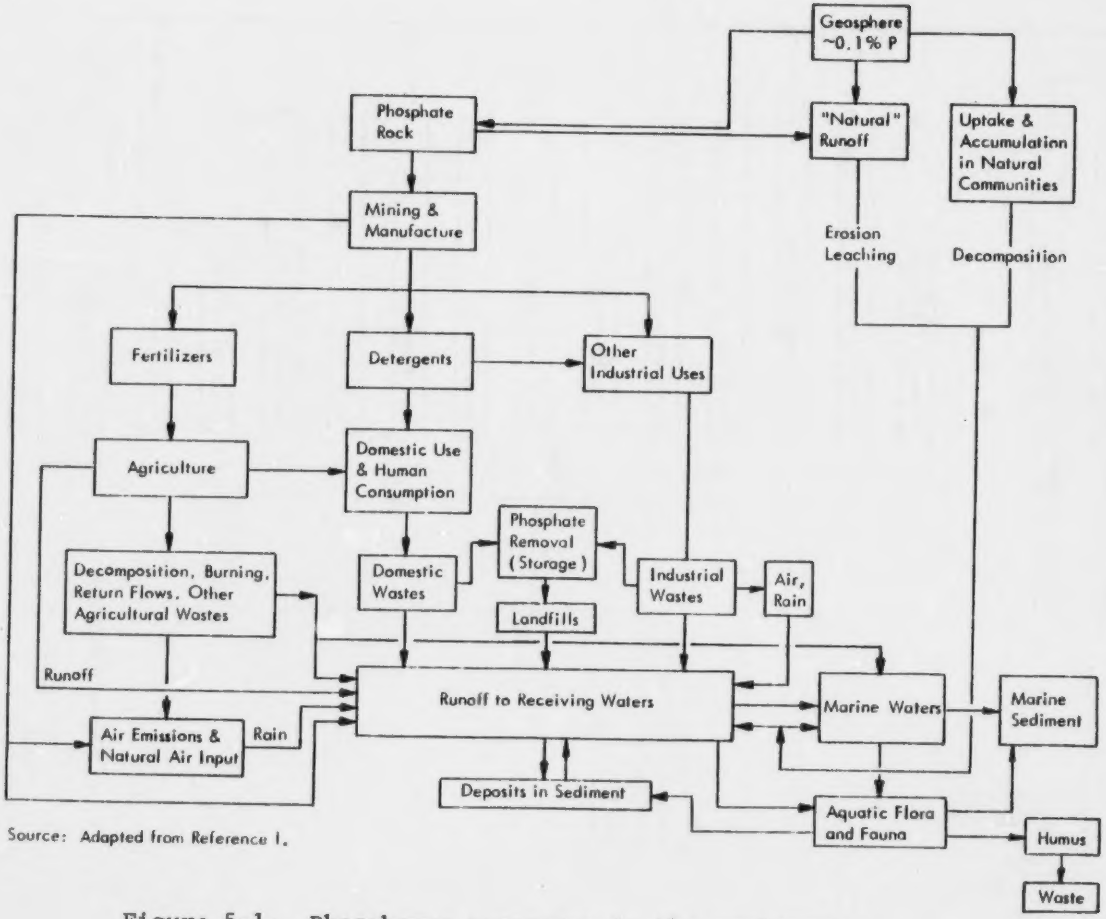
Any attempts to effectively control phosphorus discharges depend on a thorough understanding of the potential sources and quantities of these discharges and the environment they may impact. Phosphorus is an essential nutrient and is used in a wide variety of products and applications. Phosphorus in water can result from natural sources such as plants, natural runoff and erosion as well as anthropogenic sources including phosphorus manufacturing operations, agricultural and urban runoff, sewage, and industrial uses of phosphorus detergent.

This section contains a primarily qualitative discussion of the sources of phosphorus. Figure 5-1 shows the environmental cycle of phosphorus. Figure 5-2 outlines the potential phosphorus transport to receiving waters via natural and anthropogenic pathways. Natural sources are mainly nonpoint discharges while anthropogenic sources, which encompass agricultural, domestic and industrial activities, include both point and nonpoint discharges. In many cases, manufacturing industries are predominantly point sources of phosphorus discharges while the use of their manufactured products (e.g., fertilizers, food additives and animal feeds) results in predominantly nonpoint discharges.

NATURAL SOURCES

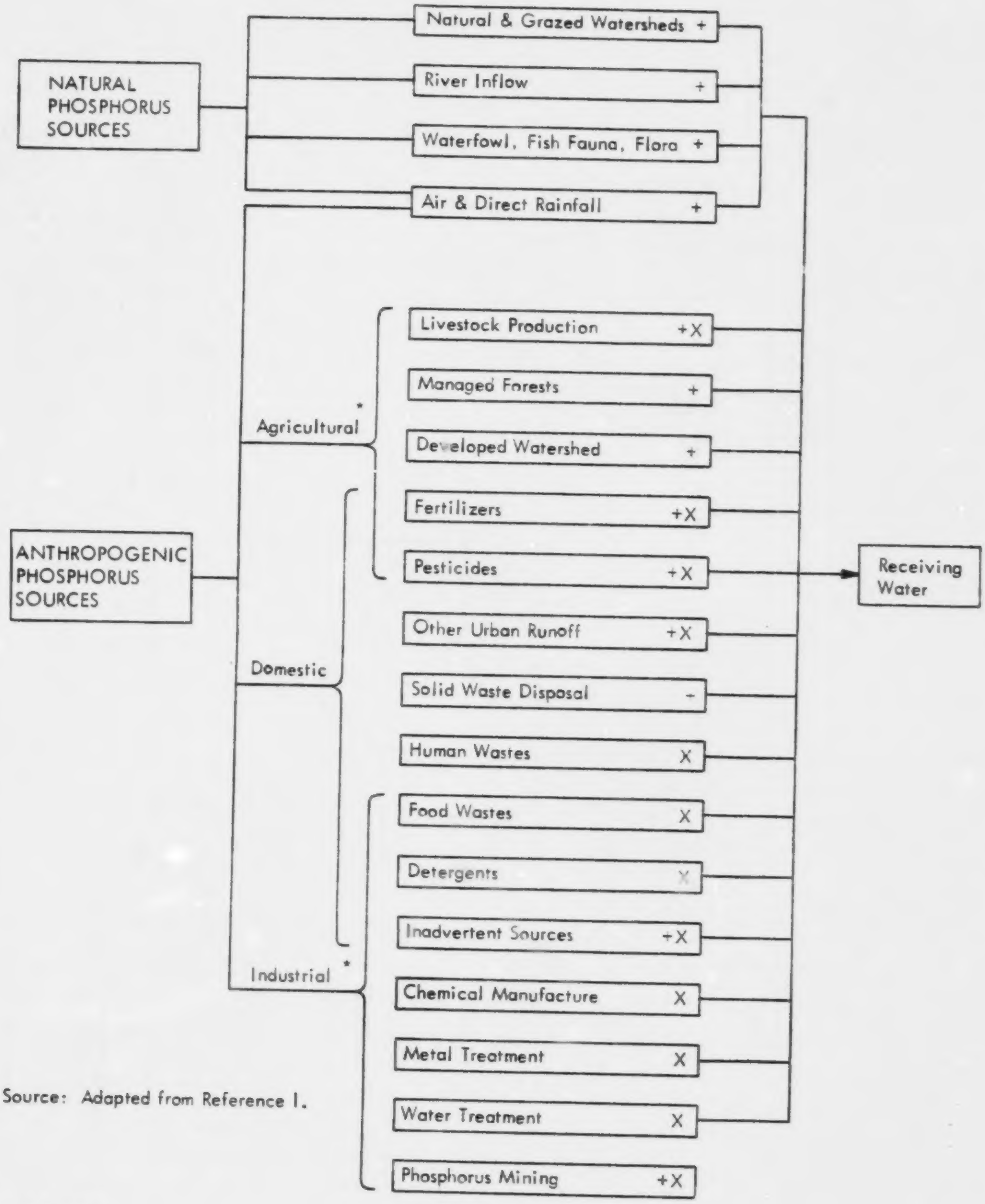
Although phosphorus is the 11th most abundant element, it comprises only 0.1% of the rocks of the earth's crust and is considered a trace element.[2] Phosphate deposits are of three types: igneous apatite deposits, sedimentary phosphorites, and guano and related biological deposits. Marine phosphorites account for almost 30% of the world's phosphate production. Phosphorus in rocks generally occurs as apatite $[Ca_{10}(PO_4)_6F_2]$ or in silicates.

Most outcroppings are the result of weathering that has dissolved the more soluble components surrounding the deposits. The weathering of phosphatic limestone and dolomite ($CaCO_3MgCO_3$) dissolves carbonates and results in a "natural" beneficiation of the insoluble apatites. Weathering of phosphatic limestone can also result in a reprecipitation of solubilized phosphate to form pebble phosphate deposits.[3] Most phosphorus outcroppings are quite stable with respect to leaching and transport except under acidic conditions.


Geosphere ~0.1% P
Phosphate Rock
"Natural" Runoff
Uptake & Accumulation in Natural Communities
Mining & Manufacture
Erosion Leaching
Decomposition
Fertilizers
Detergents
Other Industrial Uses
Agriculture
Domestic Use & Human Consumption
Phosphate Removal (Storage)
Decomposition, Burning, Return Flows, Other Agricultural Wastes
Domestic Wastes
Industrial Wastes
Air, Rain
Landfills
Runoff
Runoff to Receiving Waters
Marine Waters
Marine Sediment
Air Emissions & Natural Air Input
Rain
Deposits in Sediment
Aquatic Flora and Fauna
Humus
Waste

Source: Adapted from Reference 1.

Figure 5-1. Phosphorus transport in the environment.


NATURAL PHOSPHORUS SOURCES
Natural & Grazed Watersheds +
River Inflow +
Waterfowl, Fish Fauna, Flora +
Air & Direct Rainfall +
ANTHROPOGENIC PHOSPHORUS SOURCES
Agricultural *
Domestic
Industrial *
Livestock Production +X
Managed Forests +
Developed Watershed +
Fertilizers +X
Pesticides +X
Other Urban Runoff +X
Solid Waste Disposal -
Human Wastes X
Food Wastes X
Detergents X
Inadvertent Sources +X
Chemical Manufacture X
Metal Treatment X
Water Treatment X
Phosphorus Mining +X
Receiving Water

Source: Adapted from Reference 1.

X Point Sources
+ Nonpoint Sources
* Phosphorus Discharges May Go to Air First and Then to Water

Figure 5-2. Sources of phosphorus in receiving water.

Natural sources of phosphorus are considered to be nonpoint sources since they discharge phosphorus diffusely in general runoff. Natural discharge from native forests, prairie lands, etc., comprises the "background" phosphorus level for which there may be little means of or need for control. Other natural sources of phosphorus input to receiving waters include pollen, plant residues, wild animal and bird wastes, natural fires, leaching and both wind and water erosion from undisturbed watersheds.

Natural and grazed watersheds are uncultivated lands which may support an animal population. In some instances, a grazed watershed may become overgrazed which would lead to increased wind and water erosion. Nonpoint phosphorus from these areas is mainly a result of soil erosion. Groundwaters, including both septic systems and seepage into lakes, generally represent a negligible source of phosphorus, since most phosphorus is stabilized by precipitation, adsorption or exchange reactions with the soil.[4/]

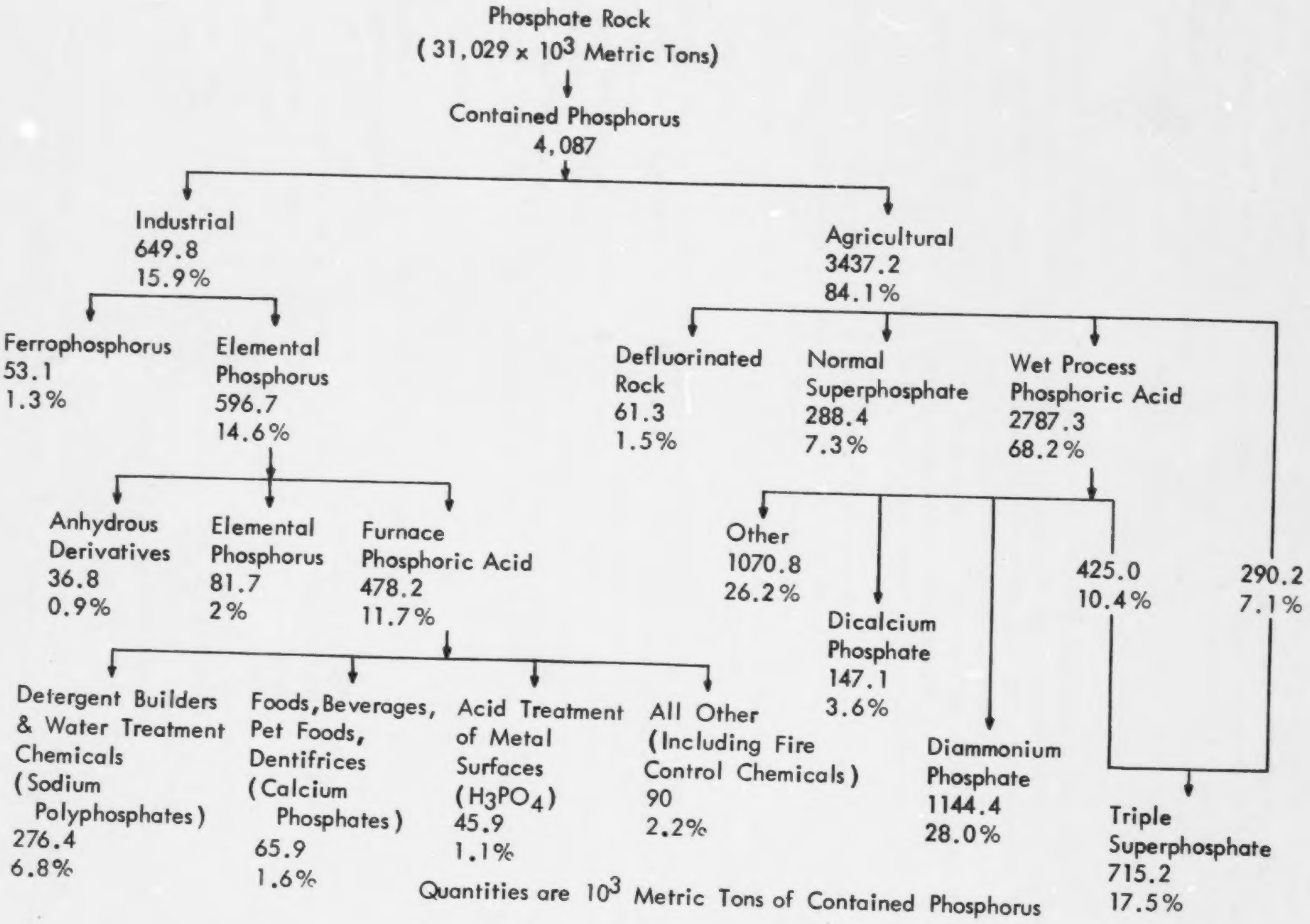
Natural sources of phosphorus in the air are small compared to phosphorus dusts and particulates from human activities. Except for phosphine in marsh gases, there are no naturally occurring gaseous forms of phosphorus.[2/] Spores and microbes suspended in the air contain some phosphorus, as do particulates generated from natural fires.

Phosphorus in direct rainfall is roughly proportional to the phosphorus-containing materials in the air. This water-scrubbing or scavenging of particles in the air will remove phosphorus either as particulate on the raindrops or as solubilized phosphorus in them. Data show higher nutrient concentrations for rainfall in and near urban areas which indicates partial--and in some cases, very significant--contribution by man,[4/] especially in areas of phosphorus-related industry, e.g., phosphoric acid and phosphate fertilizer plants.

ANTHROPOGENIC SOURCES

Anthropogenic sources of phosphorus are those generated by human activities. Most usage of phosphorus is directly related to the phosphorus mining industry. In 1975, 44.3 million metric tons of phosphate rock were mined in 16 states. Florida contributed 78% of the total with the remainder coming from Tennessee (5%), North Carolina (3%) and the western states of Utah, Wyoming, Idaho, and Montana (14%).[5/] Phosphate rock mining is a source of both point and nonpoint discharges. Except in the presence of acid rain or groundwaters, phosphorus deposits are relatively insoluble. Mining operations create greater surface areas, however, and can increase the nonpoint contributions. Any point discharges from mining operations could also have a significant effect on surrounding waters.

Figure 5-3 shows the major commercial distribution of phosphorus from mined rock. Agricultural usage (fertilizers and feeds) predominates (80%) with


Phosphate Rock
(31,029 x 10³ Metric Tons)
Contained Phosphorus
4,087
Industrial
649.8
15.9%
Agricultural
3437.2
84.1%
Ferrophosphorus
53.1
1.3%
Elemental
Phosphorus
596.7
14.6%
Defluorinated
Rock
61.3
1.5%
Normal
Superphosphate
288.4
7.3%
Wet Process
Phosphoric Acid
2787.3
68.2%
Anhydrous
Derivatives
36.8
0.9%
Elemental
Phosphorus
81.7
2%
Furnace
Phosphoric Acid
478.2
11.7%
Other
1070.8
26.2%
425.0
10.4%
290.2
7.1%
Dicalcium
Phosphate
147.1
3.6%
Detergent Builders
& Water Treatment
Chemicals
(Sodium
Polyphosphates)
276.4
6.8%
Foods, Beverages,
Pet Foods,
Dentifrices
(Calcium
Phosphates)
65.9
1.6%
Acid Treatment
of Metal
Surfaces
(H3PO4)
45.9
1.1%
All Other
(Including Fire
Control Chemicals)
90
2.2%
Diammonium
Phosphate
1144.4
28.0%
Triple
Superphosphate
715.2
17.5%

Quantities are 10^3 Metric Tons of Contained Phosphorus

Source: Reference 6

Figure 5-3. U.S. phosphorus production and domestic consumption (1975).

phosphorus detergent builders and other industrial applications comprising the majority of the remainder.[6] These three areas combined make up more than 93% of the domestic consumption of phosphorus.

With respect to air emissions, the phosphorus industry and inadvertent sources contributed 91% (63,538 MT of phosphorus) of all phosphorus air emissions in 1970[7] (see Table 5-1). Most of this was concentrated near industry; primarily the fertilizer industry. Eighty-two percent of the phosphorus-containing air emissions were attributed to the fertilizer manufacturing industry and identified as calcium and ammonium phosphates.[7] Phosphorus emitted to the atmosphere may settle onto land or water surfaces in the form of finely divided particulate matter or be removed from the atmosphere to the earth's surface by rain or other forms of precipitation. Table 5-1 lists the principal phosphorus emissions to the atmosphere from the phosphorus industry and inadvertent sources in 1970.

Particulate matter containing phosphorus, when scavenged from the atmosphere by precipitation (e.g., rain and snow), can be an important component of the phosphorus budget of natural bodies of water. Since the phosphorus content in particulate matter is relatively constant, the amount of phosphorus scavenged by precipitation is roughly proportional to the quantity of particulate scavenged or to the amount of particulates in the atmosphere.[8] It has been reported that in 1974 this source contributed one-fifth to one-third of the phosphorus entering Lake Michigan; of this amount, about 60% is attributed to the effects of man and the remainder is considered to be from natural sources.[8] As contributions to bodies of water from other sources are eliminated, the contributions from the atmosphere become more significant. A study of sources of phosphorus inputs from the atmosphere for the Chicago, Illinois, area in 1974 showed that about one-half of the phosphorus removed from the atmosphere to surface waters was in the form of orthophosphate.[8]

A summary of estimated phosphorus air emissions generated on a national basis by individual industries is presented in Section 6. This analysis shows the estimated annual quantities and percentage distribution of total phosphorus discharge as air emissions in 1978.

Agricultural Operations

Agricultural operations are mainly nonpoint sources of phosphorus resulting from the cultivation of soil, the use of fertilizers, livestock management, and the runoff associated with these activities. Rural land erosion is the prime contributor of phosphorus to the nation's waterways, with the greatest transport normally occurring during the spring thaw, snowmelt, and heavy spring rains. During the spring, the surface soil is sometimes positioned between melting snow (and/or rain) and frozen ground below. As a result, manure accumulated at the soil surface in barnyards and pastures during the winter is susceptible to transport in runoff waters. Similarly, fields

TABLE 5-1. PRINCIPAL INDUSTRY SOURCES OF PHOSPHORUS-CONTAINING EMISSIONS TO AIR - 1970

Phosphorus industry	U.S. Emission (MT P/year)[a]	% of U.S.
Triple superphosphate	15,579	22.3
Ammonium phosphate	13,397	19.2
Normal superphosphate	6,808	9.7
Fertilizer application	6,371	9.1
Rock processing	5,237	7.5
Elemental phosphorus	4,320	6.2
Inadvertent sources		
Coal combustion	9,033	12.9
Iron manufacturing	2,793	4.0
Total	63,538	90.9
Other	6,361	9.1

Source: Reference 7.

[a] Metric tons of phosphorus per year.

which are plowed and fertilized in the fall in preparation for spring planting are also vulnerable to fertilizer loss (if the chemicals are not incorporated deeply enough in the soil) and soil erosion. In addition to erosion by water transport, these cultivated fields are also vulnerable to wind erosion during dry years when vegetation or snow cover (or soil moisture--in more southern climates) is insufficient to hold the soil in place. In all of these cases, nonpoint phosphorus loading to surface waters increases.[9,10]

In agricultural watersheds, soil management practices, types of crops, and the fertility level of the eroded soil greatly influence the nutrient load from runoff. Sod or cover crops and reduced tillage can help alleviate this erosion.

The agricultural use of organophosphorus pesticides represents another nonpoint source of phosphorus. Organophosphorus pesticides are applied at rates of 2 to 14 kg of active ingredient (AI) per hectare (ha) per year in various agricultural uses.[11] Approximately 11% of the AI is phosphorus. Consequently, the total phosphorus loading to agricultural land receiving these chemicals is ~ 0.2 to 1.5 kg/ha/year. Considering the small loading per unit area, the limited mobility of phosphorus in soil, and the hydrolysis of some portion of the pesticide to esterified phosphates which are not available as plant nutrients, the contribution of phosphorus (especially orthophosphate) to nonpoint runoff from pesticide use appears to be insignificant.[1]

Most phosphorus in the soil (e.g., fertilizers, pesticides, or naturally occurring rock) may be temporarily stabilized by the formation of iron or aluminum phosphates or calcium phosphate, depending on the pH of the soil. This phenomenon reduces transport of phosphorus to groundwaters and other receiving waters. The phosphorus is carried to receiving waters by sediment (consisting of silt, clay, and organic matter) as a result of erosion of agricultural land, feedlots, forests, grasslands, etc. Organic matter is particularly susceptible to erosion because of its low density.[1] Soil erosion losses nationally have been variously estimated as about 19.8 to 27 MT/ha/year; in extreme cases, losses of 133 MT/ha/year or more are recorded.[12] Sediments (or suspended solids) are considered a pollutant in their own right, but they also represent a significant mechanism for the transport of phosphorus in the form of fertilizers and, to a lesser extent, pesticides to the nation's surface waters. Vollenweider has estimated that 1 to 5% of the fertilizer used reaches surface waters.[13]

Omernik found that from 41 to 50% of the total phosphorus in runoff from agricultural nonpoint drainages was soluble orthophosphorus (based on from 68 to 295 drainages investigated in each use category).[14]

Table 5-2 shows some values for total phosphorus watershed loading by land form and land use in the United States. The type of soil texture had a significant influence on the degree of phosphorus loading for plowed fields, grassland, and dairy pasture. The highest loading values applied for the fine textured soils. In terms of land use, the lowest phosphorus export was reported from wetlands, forests, and grasslands. The land uses which involved plowing the soil, plowed fields and truck crops, were shown to have the highest phosphorus losses. In regard to both soil texture (land form) and land use, phosphorus export was directly related to the vulnerability of the soil to erosion.[15]

TABLE 5-2. TOTAL PHOSPHORUS WATERSHED LOADING BY LAND USE AND LAND FORM IN U.S. (kg/km^2/year)

Land use	Land form					
	Fine textured		Medium textured		Coarse textured	
	Level	Sloping	Level	Sloping	Level	Sloping
Plowed fields	106	125	87	87	23	63
Grassland	23	23	10	10	10	10
Dairy (pasture)	40	63	23	23	10	10
Brush	23	23	23	23	23	23
Orchard/truck crops	125	125	125	125	125	125
Forest	10	10	10	10	10	10
Wetlands	0	0	0	0	0	0

Source: Adapted from Ref. 15.

Detergents

The use of phosphorus in detergents is a major production and consumption category. About 15% of the domestic phosphate rock supply was used in electric furnace production of elemental phosphorus in 1975 and about 58% of this phosphorus was used via phosphoric acid in the production of sodium phosphates for detergent builders and water treatment. Sodium tripolyphosphate (STPP) accounts for more than 80% of the sodium phosphates.[10] The non-STPP synthetic detergents and surfactants and the availability of STPP for use in synthetic detergents lead to the rapid replacement of soaps in the market place in the 1950's.

Phosphates are used in synthetic detergents to enhance cleaning properties. The predominant use is in powdered detergents for home laundry, but phosphates are also used in liquid and automatic dishwashing detergents and miscellaneous household cleaners. Industrial and institutional (I&I) consumption of phosphates is considerably less than the household usage. Due to the outstanding and irreplaceable properties of phosphorus in the I&I cleaners, exemptions for applications in janitorial, industrial and metal cleaning have been made in some detergent phosphate regulations.

Although phosphate detergents and cleaners represent a small volume of total phosphorus consumption compared to fertilizers, their usage is widespread and they present fairly constant input to waste treatment systems, since virtually 100% of each compound is discharged. These chemicals are a potentially controllable source and many efforts have been made to decrease phosphorus loads from detergents, including state and local phosphate detergent bans, voluntary reductions in phosphorus concentrations by manufacturers, and research and development on phosphorus substitutions.

Over the past decade, there has been a significant reduction in the phosphorus content of household laundry products in the United States. This reflects industry's reduction of phosphorus concentrations in detergents from about 12.8% in 1967 to a current 1978 average of 7.4% (Based on MRI's best estimates). Lower detergent phosphate concentrations are planned up to the early 1980's, if suitable substitutes (e.g., zeolites) are used. A phosphorus concentration of about 3% might result if zeolites enter the detergent market.17/

The main sources of phosphorus emissions from the manufacture of soaps and detergents are the spray-drying operations. In these operations, liquid formulations are dispersed into a stream of hot gas in the form of a mist of fine droplets. Moisture is rapidly vaporized from the droplets, leaving residual particles of dry solid, which are separated from the gas stream. On the average, approximately 72% of the industry's production is powdered formulations from spray dryers. Depending on the efficiency of air emissions control procedures used, this may represent a significant local source of phosphorus contamination.

Food

Some wastewaters from food processing industries, which convert agricultural crops to food products, contain high levels of phosphorus as shown in Table 5-3. For example, press water from beet sugar factories is reported to have a total phosphorus concentration ranging from 31 to 274 mg P/liter, and potato starch in wastewater results in a phosphorus level of 27 to 80.5 mg/liter.18/ Because of the high phosphorus concentrations, these wastewaters can be quite important on a local basis.

TABLE 5-3. PHOSPHORUS CONCENTRATION IN INDUSTRIAL WASTEWATERS

Type of waste	P_2O_5 (mg/liter)	Total P (mg/liter)
Beet sugar factories		
Washing water	6-30	2.6-13
Press water	71-629	31-274
Potato starch	63-184	27-80.5
Malt-house	30	13
Brewery	46.5	20.2
Slaughterhouse	18.7	8.2
Flaying-house	100	43.7
Flax retting	60	26.1
Dairy (waste volume four times the volume of milk handled)	20	8.7

Source: Adapted from Ref. 18 (as reproduced in Vollenweider, 1970, Ref. 13).

Another source of phosphorus pollution in wastewaters is food formulation and processing plants. The processing of food products which contain substantial amounts of phosphorus (i.e., meat, fish, dairy products, some vegetables) will result in losses of phosphorus to plant wastewaters. The phosphorus content of these wastewaters is further heightened by the presence of detergent used in routine washdowns of processing areas and equipment. Some losses of phosphorus-containing chemicals used in leavening systems (particularly monocalcium phosphate), antioxidants, and buffers would also be expected from food processing activities.[37] No attempt was made in this study to conduct a detailed analysis of these phosphorus sources.

Sewage

Domestic sewage contains nutrients, bacteria, and organic matter derived from human wastes which contain phosphorus from foods and pharmaceuticals, washing wastes from home laundry detergents and cleaners and automatic dishwashing compounds, wastes from residences (including garbage disposals), business, and institutions, and in many cases urban runoff. In 1970, total daily per capita contribution of phosphorus was estimated at 1.5 to 3.0 g, with phosphorus input to municipal waste treatment systems estimated to be 20% industrial and 80% residential.[13]

Table 5-4 lists household sources of phosphorus in sewage processed in municipal treatment plants. This breakdown points out the significance of both detergents and human wastes. These two sources represent consistent input to waste treatment systems. The contribution from laundry detergents and miscellaneous household sources (~ 50% of total phosphorus input) could be altered by formulation changes using phosphorus substitutes.

TABLE 5-4. PHOSPHORUS INPUT TO MUNICIPAL WASTE TREATMENT SYSTEMS FROM HOUSEHOLDS

Source	Contained phosphorus (kg/capita/year)	Reference
Laundry detergents	0.40-0.96	1, 13
Human waste	0.40-0.54[a]	1, 13, 17
Miscellaneous (garbage disposal waste, dishwater, etc.)	0.20	17
Total	1.00-1.70	

[a] Three additional values cited in Reference 13 fall within the range of these two values.

Septic Tank Systems

The most widely utilized method of on-site domestic waste disposal is the septic tank-soil absorption system.[19] The use of these systems continues to increase significantly. In 1977 over 50 million people in the United States used septic tank systems to dispose of their domestic wastes.[20]

One study on the transport of septic tank effluent to groundwater has shown that very limited phosphorus migration occurs.[21] Since much of the phosphorus is in the form of orthophosphates,[22] many types of soil particles interact with and immobilize these phosphates.[21] For example, clay materials and oxides of iron and aluminum strongly adsorb phosphates, and calcareous type (limestone) soils react with phosphorus to form hydroxyapatite. Under proper conditions, nearly complete removal of the phosphorus in septic tank wastewater occurs in the vicinity of the tile fields. The highest degree of phosphorus transport has been identified in aquifer materials comprised of coarse sand or gravel.[21] One septic system location where significant phosphorus transport might occur involves siting a septic system immediately adjacent to a water body or a stream in an unsuitable aquifer material. In the determination of appropriate sites for septic tank systems, increased emphasis should be placed on soil and groundwater characteristics.[23]

Some septic tank systems in the United States may pose a significant phosphorus pollution problem. It is not known how many septic tank systems are operated improperly or are located where they allow phosphorus to discharge to surface waters.

Other

Chemical manufacture results in point sources of phosphorus as air emissions which are generally scrubbed, or wastewater discharges which typically go to either municipal or in-house treatment. In most cases these industrial chemicals are produced from high purity electric furnace phosphoric acid. Some of the main products include food additives and animal feeds while much of the elemental phosphorus is used in manufacturing inorganic chemicals such as P_2O_5 for oil additives, insecticides, desiccants, and organic phosphorus compounds; PCl_3 for insecticide intermediates, chlorinating and reducing agents, plasticizers, and numerous other chemicals.[3,24]

Phosphoric acid and acid phosphates are used in metal cleaning, finishing and polishing. Other applications involve deoxidizers for copper and its alloys, electroplating and phosphatizing.[1] Wastewater from these operations is commonly treated in-plant for partial removal of phosphorus and other pollutants before being discharged from plant areas.[25,26]

The increase in industrial use of cooling water has resulted in greater use of water treatment chemicals containing phosphorus. Phosphorus loss from this source is generally a point source discharge to municipal treatment systems.

Human activities in urban areas contribute to both point and nonpoint phosphorus discharges. Urban runoff includes phosphorus from lawn and garden fertilizers and pesticides. Also included in this category are wastes from the nation's pet population, phosphorus deicing compounds and other small sources.

Solid waste disposal can contribute phosphorus via landfills or open dumps. Phosphorus, which contacts surrounding soils, normally undergoes reaction with the soil to stabilize the phosphorus and result in negligible transport. A few disposal sites utilize liners or other means of containment to prevent the escape of other more hazardous materials, and simultaneously prevent any possible phosphorus transport as well. With proper management, phosphorus losses from landfills and solid waste disposal can be prevented.

REGIONAL DIFFERENCES IN PHOSPHORUS DISCHARGES

According to Tennessee Valley Authority (TVA) data on regional consumption of plant nutrients (Table 5-5), 26% and 29% of total P_2O_5 in commercial fertilizers is used, respectively, in the East North Central states and in the West North Central states.[27] The South Atlantic states use about 11% of the total and 10% is applied in the West South Central states. Thus, these four regions collectively account for the consumption of about 76% of the commercial phosphate fertilizers in 1976. These data are a good indication of areas in the United States where transport of phosphate fertilizers to surface waters could be a problem. Their impact would result primarily from agricultural runoff.

Phosphate management should consider regional water quality, since areas can vary widely in their specific environmental characteristics, phosphorus problems and phosphorus sources. Regional differences are illustrated in Table 5-6 in a comparison of the phosphate sources in the Potomac River Basin, the Alafia River in Florida and Lake Erie. This is an extreme example of the diverse nutrient loading conditions which must be understood before any effective phosphate management can begin.

In 1971, detergent phosphates contributed 65% of the municipal wastewater phosphorus to the Potomac, while the mining industry was the prime source of phosphorus in the Alafia River, with only 4% of the total phosphorus load being attributed to all municipal waste.[28] Lake Erie received 35 to 50% of its total phosphorus load from detergents. These detergents comprised 70 to 80% of the total phosphorus from industrial and municipal sources. While a ban on phosphate detergents would have little impact on the amount of phosphorus entering the Alafia River, it would seem a more plausible alternative for the other two areas.

TRENDS AFFECTING PHOSPHORUS DISCHARGES

A comparison of phosphate rock usage, shown in Table 5-7 for 1972, 1973, and 1974, shows a relatively constant distribution through all product categories. Projections for phosphate rock consumption through 1980 show increases in the major categories; their percentages of the total, however, are fairly constant.[29] The total is expected to increase from 3.2 to 4.1 to 4.2 million metric tons of phosphorus, with fertilizers, builders and water treatment chemicals, and feeds comprising approximately 77, 8.1, and 8.6%, respectively.

TABLE 5-5. ESTIMATED REGIONAL CONSUMPTION OF P_2O_5 IN COMMERCIAL PHOSPHATE FERTILIZERS APPLIED IN 1976

Region or state	States included in region	Total fertilizer P_2O_5 consumed, % of total for U.S.
New England	Maine, New Hampshire, Vermont, Massachusetts, Rhode Island, Connecticut	0.75
Middle Atlantic	New York, New Jersey, Pennsylvania, Delaware, Maryland, West Virginia	4.75
South Atlantic	Virginia, North Carolina, South Carolina, Georgia, Florida	10.66
East North Central	Ohio, Indiana, Illinois, Michigan, Wisconsin	25.82
West North Central	Minnesota, Iowa, Missouri, North and South Dakota, Nebraska, Kansas	29.04
East South Central	Kentucky, Tennessee, Alabama, Mississippi	7.59
West South Central	Arkansas, Louisiana, Oklahoma, Texas	10.13
Mountain	Montana, Idaho, Wyoming, Colorado, New Mexico, Arizona, Utah, Nevada	5.11
Pacific	Washington, Oregon, California	5.58
Alaska	Not applicable	0.01
Hawaii	Not applicable	0.44
Puerto Rico	Not applicable	0.12
Total		100.00

Source: Adapted from Reference 27.

TABLE 5-6. REGIONAL VARIATIONS IN PHOSPHATE LOADING

	Municipal (%)	Industrial (%)	Land runoff (%)
Potomac River	78.0	8.6	13.4
Alafia River	4.0	96.0	-
Lake Erie	68.5	7.3	24.2

Source: Reference 28.

TABLE 5-7. ANNUAL TRENDS IN PHOSPHORUS PRODUCTS
(x 10^3 MT phosphorus)

Use/year	1972	%	1973	%	1974	%
Fertilizer	9,355	80	9,818	79	10,914	79.4
Detergents and waste-water chemicals	936	8	915	7.4	1,017	7.4
Animals feeds	467	4	544	4.4	605	4.4
Foods	467	4	544	4.4	605	4.4
Other	467	4	544	4.4	605	4.4
Total	11,692		12,365		13,746	

Source: Reference 29.

Production in 1976 showed a decline in thermal phosphoric acid (following a sharp decline in 1975) with a subsequent increase in wet-process acid production.[30] The thermal process requires large amounts of electrical power; therefore, increasing power costs have made this process economically unattractive. Triple superphosphate was stable, normal superphosphate declined, and ammonium phosphates were showing continued growth.

Efforts have been made to improve the purity of wet-process acid since the dry process requires additional pollution control equipment and approximately five times as much energy.[5] Although the purity of wet-process acid is generally not high enough for food applications, it can be used in detergents, and animal feeds. These data are consistent with earlier projections which showed wet-process phosphoric acid as the main source of growth in the fertilizer industry.

The usage of builders and wastewater chemicals reflects the soap and detergent industry trends to reduce phosphorus concentrations in their products.

CURRENT ACTIVITIES

The 1972 Great Lakes Water Quality Agreement between the United States and Canada is an attempt to restore and enhance the water quality of the Great Lakes. The control of phosphorus entering the Great Lakes is a major activity under this agreement.[31-33] Emphasis has been placed on reducing the phosphorus concentration in detergent formulations, evaluating nonpoint source discharges and possible solutions, and controlling point sources by placing a 1 mg/liter phosphorus limit on municipal treatment plant effluents in the lower Great Lakes Basin (plants with a capacity greater than 1 million gallons per day). Extensive surveillance programs have been active in obtaining data which are used to formulate recommendations and implementation programs. Most recommendations to the International Joint Commission (IJC) include continued and increased monitoring programs (for both point and nonpoint sources) along with additional efforts to remove phosphorus and develop alternative builders. The data resulting from these endeavors should continue to increase the understanding and control of eutrophication in the Great Lakes and other areas as well.

The Research Advisory Board of IJC established a phosphorus task force to identify more accurately the phosphorus sources draining into the basin states and evaluate control methods. This should be a significant source of continuing data on phosphorus loading.

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SECTION 6

QUANTIFICATION OF PRINCIPAL PHOSPHORUS SOURCES

The principal sources of phosphorus released to the environment were described in Section 5. The quantitative results of this study are presented and discussed in this section.

The quantification study discussed in this section has resulted in estimates of quantities of total phosphorus discharged to the environment. An exhaustive study of every phosphorus source was beyond the scope of this report. Thus, some minor sources of phosphorus emission were not addressed in these quantification estimates.

RESULTS OF THE NATIONAL ASSESSMENT

The methodology and results of the quantification of phosphorus emissions from nonpoint and point sources are presented in the following subsections.

Nonpoint Sources of Phosphorus

A draft report, "National Assessment of Water pollution from Nonpoint Sources", was completed in 1975 for the EPA.[1/] That study was conducted in two phases: (a) development of loading functions and (b) calculation of nonpoint pollution loads for the United States. The report addressed the following pollutants: nitrogen, phosphorus, BOD, sediment, coliforms, radioactivity, salinity, heavy metals, acid mine drainage, and pesticides. The results of that report were used as the principal data base for nonpoint sources in this study.

For purposes of this study, the discussion is limited to pollutants which are actually delivered to surface waters. Pollutants that are transported within a land source, but never reach surface waters are not considered. In addition, pollutants transported to subsurface waters that are not a part of the surface water inventory are not classified in this study.

Methodology and Results for Estimating Nonpoint Emissions--

A brief discussion of the methodology used and results obtained in estimating the phosphorus emissions from nonpoint sources follows under separate headings.

Cropland, pasture and rangeland, and forestland--Emissions of phosphorus from these sources were calculated by an approach in which the estimated quantities of phosphorus contained in eroded sediments were summed for the various sources. The analysis was based on the Universal Soil Loss Equation (USLE), which predicts soil loss from sheet and rill erosion. The USLE contains parameters which account for the influence of rainfall, erodibility of soils, topography, and the nature of ground cover and cultural practices.[2] Data on these parameters were obtained from numerous sources, notably U.S. Department of Agriculture (USDA) compilations of information on soils, topography, soil cover, and tillage or management practices. The phosphorus content of soils for the United States was taken from data for P_2O_5 concentrations in the top 30 cm (1 ft) of soil in the 48 conterminous states.[3]

Although more than 30 years old, these data for the broad general regions of the country were within the same ranges as later data of this type reported in selected soil surveys conducted since 1946. Analysis of fertilizer usage patterns indicated that the contribution of phosphorus to nonpoint loads through fertilizers was small compared to the contributions from phosphorus originally in the soil. The analysis also showed that fertilization is required to maintain natural phosphorus concentrations in soils.

The phosphorus concentration of eroded sediments is increased relative to that observed in the original soil, since an enrichment of phosphorus content occurs during transport. An enrichment factor of 1.5 was employed uniformly in the calculations. Enrichment implies that phosphorus is preferentially associated with the more erodible, fine-grained soil particles which are in greater abundance in sediment.

Not all soil lost from a field is delivered to a body of water. For this reason, a delivery ratio of less than one was used to reduce soil loss (and consequently, phosphorus) to a smaller value actually delivered to streams. The delivery ratio was estimated on an area-by-area basis as a function of distance to streams and soil properties. The delivery ratio used represents delivery to the edge of receiving streams. In-stream processes, such as sedimentation and benthic accumulation, were excluded from the study. Thus, the estimated phosphorus loads tend to be larger than those measured at the mouth of a watershed, particularly when the drainage area in the watershed is large.

The other major data required consisted of area-by-area information on land uses, such as areas and types of cropland and data on soils, topography, cover and related factors. The land use and conservation practices were obtained from the USDA's Soil Conservation Service, 1967 Conservation Needs Inventory.

In summary, the method used to estimate nonurban, nonpoint loads of phosphorus was based on the premise that phosphorus is primarily delivered to streams in a nonsoluble form which accompanies eroded sediments. The amount of delivered sediment was estimated using the USLE modified by a delivery function; the phosphorus content of delivered sediments was calculated from soil phosphorus concentrations modified by an enrichment factor. Land use and related information were obtained principally from the 1967 Conservation Needs Inventory. The smallest land unit considered was the county; loads were estimated for each county for a variety of land uses and then aggregated to larger units (i.e., states).

The estimated pollution loads from cropland, pasture and rangeland, and forestland are summarized in Table 6-1. A brief discussion of factors contributing to nonpoint phosphorus pollutant loads by specific source follows.

Erosion of soil and associated organic matter following agricultural cultivation is an extensive source of water pollution.[1] Farmland was classified in terms of row crops, close grown crops, rotation hay and pasture, hayland, orchards, and temporarily idled cropland. This source represents approximately 480 million acres of land area in the continental United States.[1]

The extent of sediment erosion from cropland varies in response to a number of variables: type of crop; rainfall and runoff; soil characteristics; topography; type of tillage; and conservation practice. Sediment acts as a transport agent for potential pollutants such as plant nutrients (e.g., phosphorus and nitrogen), crop residues containing organic matter, and pesticides containing phosphorus. Compounds of phosphorus may be either absorbed on, or initially existing in soil particles. Thus, if the soil is eroded into a water course, phosphorus may be carried along and contribute to pollution of water.

Approximately 211 million hectares of land area in the continental United States are used as grassland pasture and range.[1] This acreage, as defined in this study, also includes acres in farmsteads and country roads.

Well-managed pasture and rangeland can provide good cover which protects soil from erosion. Releases of sediment and other pollutants from land in these uses are, therefore, generally low when compared to those for cropland. Sources of phosphorus in pasture and rangeland runoff include animal wastes, organic matter, and phosphorus bound in the eroded soil.

Forestlands are treated as a combination of recently harvested forest, logging roads, undisturbed commercial forest and noncommercial forests.[1] Pollutant loads from forested lands are expressed in this report as a single load for all of these subclasses.[1] Sources of phosphorus in forestland runoff are organic matter (e.g., leaves, decaying vegetation, and humus), wild animal wastes, and phosphorus bound in the eroded soil. As with other categories of

Table 6-1. ESTIMATED NATIONAL NONPOINT SOURCE DISCHARGES OF TOTAL PHOSPHORUS TO THE ENVIRONMENT IN PRECIPITATION RUN-OFF AND AIR EMISSIONS IN 1978

	Estimated discharges to environment			
	Discharged to water[1/]			
Source activity or area	MT of total P/year (rounded to nearest 100 tons)	Land area (10^6 ha)	Kilogram of P/ ha/year	Air Emissions[4/] (MT of total P/year)
A. Runoff discharges				
Cropland	1,433,400	195.3	7.34	Data not applicable
Pasture and rangeland	985,600	211.1	4.67	Data not applicable
Forestland	84,300	246.1	0.34	Data not applicable
Livestock feedlots	28,700	0.0836	343.30	Data not applicable
Urban runoff	18,400	6.1	3.02	Data not applicable
Roadway runoff	1,000	Not available	Not available	Data not applicable
Subtotal	2,551,400	-	-	
B. Inadvertent sources				
Windblown soil	Data not applicable			6,300
Fertilizer application (field spreading)	Data not applicable			4,800
Agricultural burning	Data not applicable			3,600
Forest fires	Data not applicable			6,700
Subtotal				21,400
National total, nonpoint source	2,551,400	-	-	21,400

Sources: References 1 and 4.

land use, the primary mode of phosphorus transport is the erosion of soil and associated organic matter both of which contain phosphorus.

Livestock feedlots--Estimates of phosphorus emissions from feedlots included only those feedlots smaller than 1,000 head of beef cattle or equivalent numbers for other animals in confined feeding. The larger feedlots were considered to be point sources regulated by point source guidelines.[1/]

The basic method consisted of: (a) a method to estimate runoff from feedlots based on precipitation characteristics of a region; (b) selection of representative values, from published data, of concentrations of phosphorus in feedlot runoff; (c) calculation of feedlot sizes (areas, and numbers of livestock) from information on numbers of livestock on feed in lots of different sizes in the smallest or most representative geographic or political area; and (d) summation of the area or regional loads to the appropriate areas, such as the state.

Uncontrolled livestock feedlots are sources of concentrated wastes and, if improperly managed, these wastes can result in substantial pollution loads. The emission data shown in this report (Table 6-1) apply to uncontrolled feedlots (i.e., 1,000 head or less).

Animal wastes deposited on the surface of feedlots are usually accumulated and compacted by movement of the livestock, and are transported beyond the feedlot site whenever storm runoff occurs. Several factors affect the magnitude and quality of such runoff: storm intensity and duration; antecedent moisture condition; nature of the feedlot surface, and the density of animals per unit area.[1/]

During runoff, pollutants on the feedlot surface are dislodged and transported either in solution or in suspension toward a discharge point, such as a stream, lake, or reservoir. Because of trapping, interception, and other obstacles, some of the suspended pollutant in runoff does not reach the surface waters. Also, phosphorus pollutants in solution are, in part, trapped or otherwise attenuated because of percolation and leaching. Therefore, the net loads delivered are always smaller than the amounts of pollutants generated on the feedlot site.[1/]

Urban runoff--The basic source of information for urban runoff was several studies on the rates of deposition and subsequent wash-off of pollutants in representative urban areas. Available data were categorized for different urban land uses--residential, commercial, light and heavy industry, and open land. Demographic, urban land use characteristics, and urban area data were employed to calculate street lengths (expressed as curb-miles) for urban areas. Loading data per curb-mile derived for the various urban land uses were combined with street curb lengths to calculate loadings of phosphorus for each urban center. An urban area was defined as an incorporated town or city having a population of 25,000 or more in the 1970 census.

The pollutant loads carried in the urban runoff have been estimated for 847 cities.1/ These cities comprise a total land area of about 14.7 million acres. Table 6-1 shows the total estimated phosphorus loading from urban runoff.

Urban storm water may pick up wastes on both pervious and impervious surfaces and, thereby, contribute to pollution of receiving waters. The origins of this phosphorus pollution in urban areas are discarded litter, automotive exhaust and fuel leakage, organic debris from tree leaves and grass trimmings, dust and fly ash from industrial facilities, lawn fertilizer and pesticides, pet wastes, etc.

Rural roadway runoff--A phosphorus deposition rate (1.44×10^{-6} lb of phosphorus) per axle-mile was employed in calculation of phosphorus emissions from roadways. Other needed data were miles of highway by state or other region of interest, and highway traffic volumes. The traffic data were obtained from the Federal Highway Administration and from state reports of vehicular traffic. In Texas and California, for example, daily rural vehicular traffic mileages for the period of record were 132 and 141 million miles, respectively.

Combination of such data along with the distribution of vehicle types were used to generate axle-mile estimates, which were multipled by the above specified phosphorus deposition rate to calculate phosphorus emissions.

Table 6-1 shows the estimated phosphorus loading from rural roadway runoff. The runoff from highways and highway rights-of-ways contains significant amounts of oil, fuel residues, heavy metals, dust and dirt, tree leaves and grass trimmings. The sources of these pollutants may be: vehicles, road surface materials, atmospheric fallout, erosion and runoff from adjacent areas, litter and spills.1/ The study1/ estimated phosphorus pollutant deposition relative to use of rural roadways by motor vehicular travel.

Air Pollution from Nonpoint Phosphorus Sources--

Inadvertent sources account for the significant phosphorus air emissions in the nonpoint category as shown in Table 6-1.

The data base used in this assessment of phosphorus air emissions from nonpoint sources was taken from Reference 4. These data were updated so as to apply as estimated values for 1978. The updating procedure consisted basically of adjusting the emissions level to correspond by direct proportion to the estimated changes in consumption of phosphorus-based material from the base year (1973) to 1978.

Data obtained from the literature indicate that the field spreading of phosphate fertilizers accounts for an air emission rate of 2 kg P_2O_5/metric ton (MT)* of applied fertilizer.[5] In 1978, the estimated total field application of normal superphosphate, triple superphosphate and the ammonium phosphates was 5,530,000 MT.

Since P_2O_5 is 43.64% phosphorus, the estimated total phosphorus emission to the air due to field spreading is approximately 4,800 MT/year calculated as $\left(\frac{2 \times 5{,}530{,}000 \times 0.4346}{100}\right)$.

Comparison of Estimated Nonpoint Emissions with PLUARG Data--

The methodology used to estimate phosphorus loads from rural areas involves numerous assumptions and provides only long-term average results. Generally, phosphorus loads for most watersheds are not available in the United States. However, considerable work has been done in the Great Lakes Basin. It is, therefore, interesting to compare the results obtained there with those estimated in this report.

For the Great Lakes Basin, the MRI National Assessment[1] obtained the following unit loads:

Cropland	3.55 kg/ha/year
Pasture/range	2.57 kg/ha/year
Forest	0.1 kg/ha/year

In 1978, the International Reference Group on Great Lakes Pollution for Land Use Activities (PLUARG) reported[6] the following ranges of measured values for their pilot watersheds:

Crop	0.2-4.6 kg/ha/year
Improved pasture	0.1-0.5 kg/ha/year
Forested/ woodland	0.02-0.67 kg/ha/year

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* Throughout this section, values will be given in terms of kg/metric ton (MT). Phosphorus conversion factors pertinent to the calculations in this section are given in Appendix A. Descriptions of the typical methodology used to calculate the estimated total phosphorus emissions from industrial point sources are presented in Appendix B.

The MRI estimates fall within the observed range for cropland and forest; the estimate is higher for pasture and range. This generally good agreement lends credibility to the methodology used in the assessment. However, in comparing the two sets of numbers, two facts should be kept in mind. First, the PLUARG results are based on 2 years of data; the MRI results are long-term statistical averages generated for use with the Universal Soil Loss Equation. The PLUARG report noted that a single large storm in the Maumee Basin caused a 100-fold increase in sediment yield in 1975 as compared with 1976.[6/] Since observed sediment/phosphorus yields in a watershed are intimately connected to the character of the actual rainstorms involved, short-term averages can give misleading results, either high or low, as compared with a long-term average. Second, the MRI results are loadings to the nearest streambank; PLUARG measured rivermouth loads, which should be smaller (substantially so, if the watersheds involved are large).

Point Sources of Phosphorus Discharge

The major point sources of phosphorus discharge to the environment, discussed in Section 5, are quantified on an estimated basis in this section. The aggregate of these industrial point source discharges and municipal effluents is estimated to account for at least 93% of the total phosphorus discharge from all United States phosphorus-consuming industries. The 21 point sources which were addressed in this study and the corresponding SIC numbers are shown in Table 6-2.

Each activity listed in Table 6-2 is evaluated and discussed in the following subsections. Each analysis includes a process flow diagram, a brief discussion of process technology and mass balance, and a description of the nature and estimated emission factors for phosphorus discharges to the environment in wastewater, atmospheric emissions and solid wastes. Finally, a national emission estimate, which quantifies principal point sources, is developed and described. The results for all national point sources are presented in Table 6-17, p. 157.

All data on quantification of phosphorus sources are presented in terms of total phosphorus (i.e., kilogram of total phosphorus per metric ton of product). All quantification estimates apply for 1978.

Mining and Beneficiation of Phosphate Rock (SIC No. 1475)--

Phosphate rock mining and processing is conducted in four regions of the United States. The reported contribution of each area to the total output for 1975 is: (a) Florida, 78%; (b) North Carolina, 5%; (c) Tennessee, 5%; and (d) Western States (Utah, Wyoming, Idaho, and Montana), 12%.[7/]

TABLE 6-2. POINT SOURCES OF PHOSPHORUS EMISSIONS TO AIR AND WATER

SIC No.	Point source activity
	Commercial production industries
1475	Mining and beneficiation of phosphate rock
2874	Wet-process phosphoric acid
2874	Superphosphoric acid
2874	Normal superphosphate
2874	Triple superphosphate
2874	Ammonium phosphate
2048	Defluorinated phosphate rock (livestock and poultry feeds)
2048	Animal-feed-grade calcium phosphates
2819	Elemental phosphorus
2819	Dry-process phosphoric acid (furnace process)
2819	Phosphorus pentoxide
2819	Phosphorus trichloride
2819	Phosphorus oxychloride
2819	Phosphorus pentasulfide
2841	Sodium phosphates
2819	Food-grade calcium phosphates
2841	Laundry detergents (phosphorus-based)
2819	Direct acid treatment of metal surfaces
2819	Phosphorus-based water treatment chemicals
None	Municipal sewage treatment
None	Inadvertent sources
None	Food processing

Source: Ref. 8.

Domestic operations are categorized by type of production as (a) Eastern processes and (b) Western processes. These operations are discussed below under separate headings.

Eastern processes--A representative flow diagram describing this process is shown in Figure 6-1; process details are discussed in Reference 7.

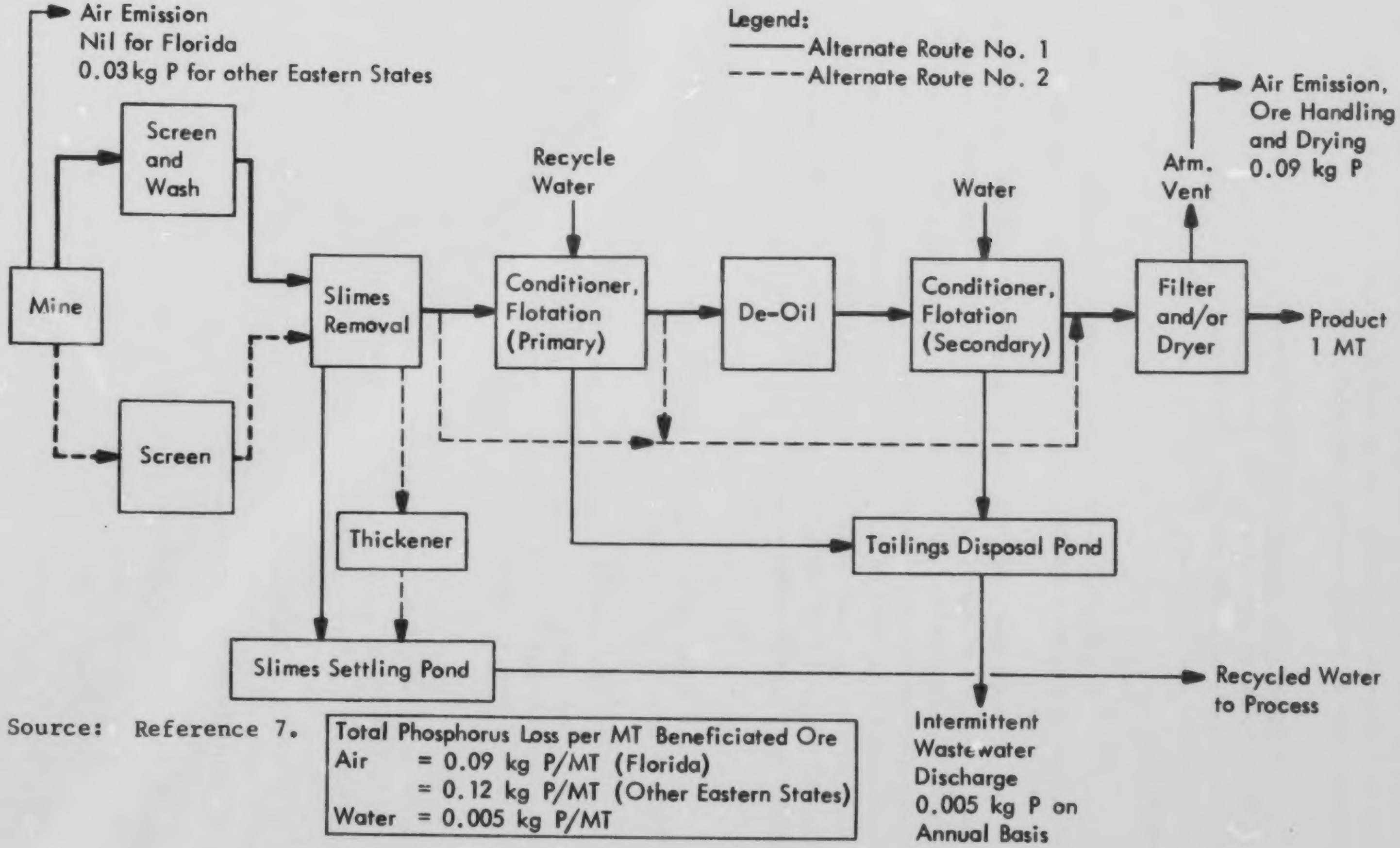
Effluent wastewater7/--Wastewater streams associated with Eastern phosphate rock production are shown below.

Waste	Source	Disposition
Primary slimes (3 to 5% solids)	Desliming cyclones	Settling ponds
Secondary slimes	Holding tanks, secondary desliming	Settling ponds
Sand tailings (20 to 30% solids)	Flotation cells	Mined out areas for land reclamation
Mine pit seepage	Mine	An intermittent and indeterminate volume discharged to a slimes or tailings waste stream
Dust scrubber slurry	Dryers	Discharged to waste streams

The treatment of process wastewater streams consists basically of gravity settling through the extensive use of ponds.

Effluents are intermittently or continuously discharged from the pond settling area by the ore beneficiation facilities. The discharged volumes of effluents are affected by (a) the degree of water reuse in processing, (b) total amount and frequency of rainfall, (c) surface runoff, and (d) available settling pond capacity.

Effluents typically include not only excess water from the process recycle system, but also various quantities of incidental water. An analysis of data for a total of 18 eastern facilities (located in Florida, Tennessee and North Carolina) shows that the average discharge of total phosphorus (as phosphate) amounts to 0.047 kg/MT beneficiated ore. It is assumed that 50% of the producers discharge and that because of rainfall patterns, this discharge occurs for a period of 2.5 months each year (Martin, W., Personal Communication,


Air Emission
Nil for Florida
0.03 kg P for other Eastern States
Legend:
Alternate Route No. 1
Alternate Route No. 2
Mine
Screen and Wash
Screen
Slimes Removal
Recycle Water
Conditioner, Flotation (Primary)
De-Oil
Water
Conditioner, Flotation (Secondary)
Atm. Vent
Air Emission, Ore Handling and Drying 0.09 kg P
Filter and/or Dryer
Product 1 MT
Thickener
Tailings Disposal Pond
Slimes Settling Pond
Recycled Water to Process
Intermittent Wastewater Discharge 0.005 kg P on Annual Basis

Source: Reference 7.

Total Phosphorus Loss per MT Beneficiated Ore
Air = 0.09 kg P/MT (Florida)
= 0.12 kg P/MT (Other Eastern States)
Water = 0.005 kg P/MT

Figure 6-1. Flow diagram for phosphate mining and processing--Eastern states.

EPA, Effluent Guidelines Division, Washington, D.C., January 1978). Thus, estimated phosphorus discharge on an annual basis is about 0.005 kg phosphorus per metric ton of beneficiated phosphate ore.

Atmospheric emissions--Emissions occurring during mining and benefication of eastern phosphate ore were estimated on the basis of data in Reference 5. These data are summarized in Table 6-3. Except where otherwise noted all subsequent calculations on atmospheric emissions were made by the following methods.

Mining--The wet mining operations used for Florida land-pebble phosphate rock produce essentially no particulate or phosphorus emissions.

In open-pit mining of hard rock phosphate in Tennessee and North Carolina, the ore mining, loading and hauling cause air emissions of small amounts of phosphate rock particulates. Assuming the P_2O_5 content of particulates emitted to the air to be the same as that in the phosphate ore, this air emission can be estimated in the following manner. The uncontrolled particulate emission factor is 0.25 kg/MT of beneficiated ore, the P_2O_5 content in the ore is 26% and there is no emission control. Thus, the phosphorus emission can be estimated to be approximately 0.03 kg phosphorus per metric ton of beneficiated ore.

Beneficiation--Phosphorus air emissions occurring in the beneficiation process are estimated as follows.

For ore handling, the uncontrolled particulate emission factor is 0.5 kg/MT product, the P_2O_5 content in the emission is 30%, and the level of emission control is 50%. The estimated emission is 0.03 kg phosphorus per metric ton of beneficiated ore.

For drying of the phosphate rock concentrate, uncontrolled emissions are 7.5 kg particulate per metric ton of beneficiated phosphate ore, the particulate contains 30% P_2O_5, and the emission control is 94%. The estimated emission is 0.06 kg phosphorus per metric ton of beneficiated ore.

Summary of phosphorus losses to environment--Data on phosphorus losses to the environment from Eastern phosphate mining and processing (basis, 1 MT of beneficiated ore) follows:

Total atmospheric losses for Florida	0.09 kg P/MT
Total atmospheric losses for other Eastern states	0.12 kg P/MT
Total wastewater losses for all Eastern states	0.005 kg P/MT

TABLE 6-3. SOURCES AND ESTIMATES OF PHOSPHORUS-CONTAINING AIR EMISSIONS FOR EASTERN AND WESTERN PHOSPHATE ROCK MINING AND BENEFICIATION

Production activity	Uncontrolled particulate emission factor (kg/MT)	% P2O5 in emissions	Estimated level of emission control (%)	Total phosphorus emissions--after controls (kg P/MT product)		Comments
Eastern producers						
Mining	0.25	26	0	0.03		Not applicable to Florida wet-mining operations
ore handling	0.5	30	50	0.03		
Drying	7.5	30	94	0.06		
Total				0.12		
				Route No. 1[a]	Route No. 2[a]	
Western producers						
Mining	0.25	26	0	0.03	0.03	
Crushing and grinding	10	30	97	0.04	0.04	
Drying	7.5	30	94	0.06	NA	
Calcining-cooling	20	30	95	NA	0.13	
Total				0.13	0.20	

Source: Ref. [illegible].

[a] See Figure 6-2.

Western processes--Figure 6-2 presents a description of the representative mining and beneficiation operations for Western producers. Details of this process are discussed in Reference 7.

Effluent wastewater--The raw waste loads from the Western processes consist of slimes and tailings which are sent to settling ponds. For the water recycle process, the high net evaporation rate which applies for this region of the United States makes it feasible for these plants to have no discharge of wastewater effluent to the environment. In the mining area around all plants, the only wastewater occurring is normal surface runoff. Thus, it is concluded that there is essentially no discharge of effluent wastewater by Western producers.

Atmospheric emissions--Emissions which occur during Western phosphate rock mining and beneficiation operations were estimated on the basis of data taken from Reference 5. The calculation methods were the same as those described earlier for Eastern producers. Emission data developed in these estimates are summarized in Table 6-3. The estimated total air emissions are 0.13 and 0.20 kg phosphorus per metric ton of beneficiated ore for Route Nos. 1 and 2, respectively. The process steps used in routes are shown in Figure 6.2.

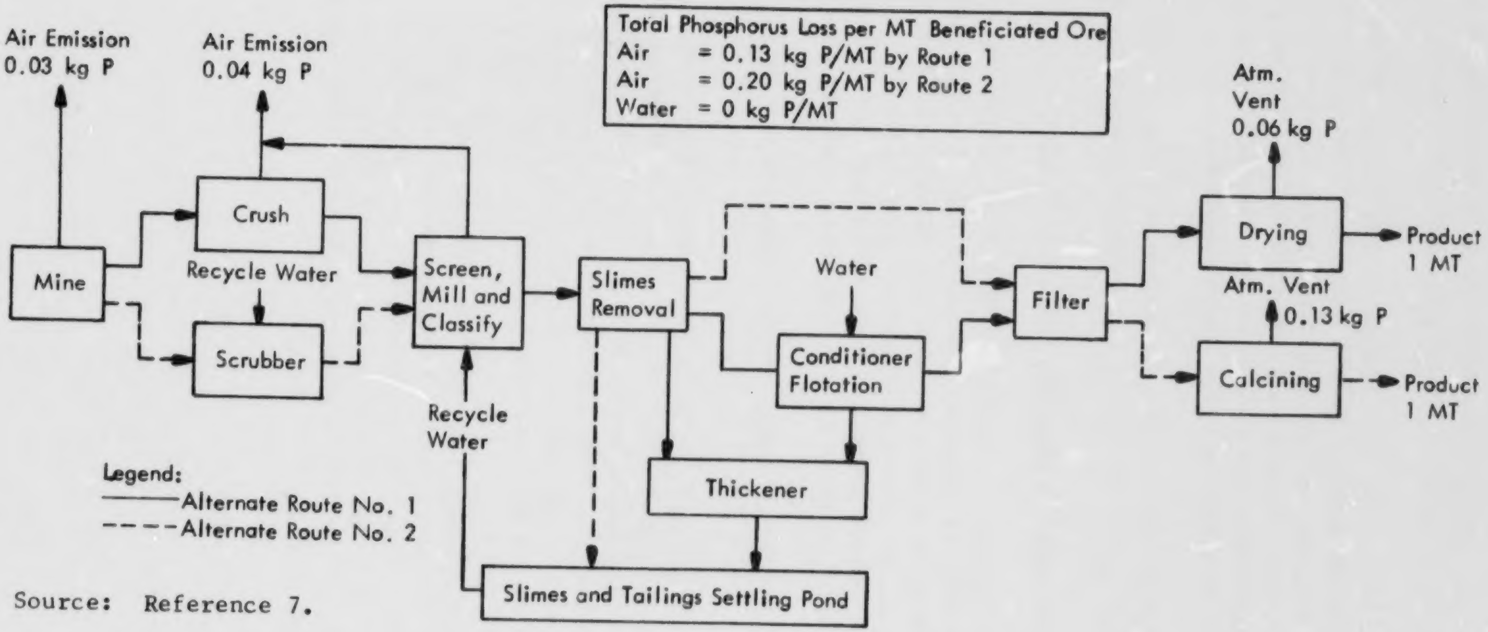
Summary of phosphorus losses to environment--Data on phosphorus losses to the environment from Western phosphate mining and processing (basis, 1 MT of beneficiated ore) follows:

Total atmospheric losses	
Route No. 1 (Figure 6-2)	0.13 kg P/MT
Route No. 2 (Figure 6-2)	0.20 kg P/MT
Total wastewater losses	0 kg P/MT

National emissions for mining and beneficiation of phosphate rock--In 1976 the total domestic marketable production of phosphate rock was reported to be 44,451,800 MT (49 million short tons).[9] Production is estimated to increase to 56,245,200 MT (62 million short tons) in 1980.[9] Assuming a uniform growth rate from 1976 to 1980, the production level for 1978 can be estimated to be 50,348,000 MT (55.5 million short tons).

For all Eastern operations, the emission loss in wastewater can be estimated as approximately 220 MT phosphorus per year. There is no discharge of effluent wastewater from the plants of Western producers.[7]

There are no significant air emissions from Florida wet-mining operations.[7] In North Carolina and Tennessee, the open-jet-mining of hard rock creates some air emissions. Also, the ore handling and drying operations for all Eastern ores contributes to phosphorus air emissions. Thus, the total air


Air Emission
0.03 kg P
Air Emission
0.04 kg P
Total Phosphorus Loss per MT Beneficiated Ore
Air = 0.13 kg P/MT by Route 1
Air = 0.20 kg P/MT by Route 2
Water = 0 kg P/MT
Atm.
Vent
0.06 kg P
Mine
Crush
Recycle Water
Scrubber
Screen, Mill and Classify
Slimes Removal
Water
Conditioner Flotation
Filter
Drying
Product
1 MT
Atm. Vent
0.13 kg P
Calcining
Product
1 MT
Recycle Water
Thickener
Slimes and Tailings Settling Pond
Legend:
Alternate Route No. 1
Alternate Route No. 2

Source: Reference 7.

Figure 6-2. Flow diagram for phosphate mining and processing--Western states.

emissions factor is 0.12 kg phosphorus per metric ton of beneficiated ore (Table 6-3). The overall phosphorus discharge (air emission) for Eastern operations can be estimated to be 5,320 MT phosphorus per year.

For Western operators, it was assumed (Lehr, J. R., Personal Communication, Tennessee Valley Authority, Muscle Shoals, Alabama, October 1977) that about 70% of the operations use the alternate process route and that 30% use the regular process route (Figure 6-2). On this basis, the weighted emission factor is 0.18 kg phosphorus per metric ton of beneficiated ore. Thus, the estimated annual air emission is 1,100 MT phosphorus.

The total wastewater emissions are estimated to be 220 MT phosphorus annually and the estimated air emissions are 6,420 MT phosphorus per year.

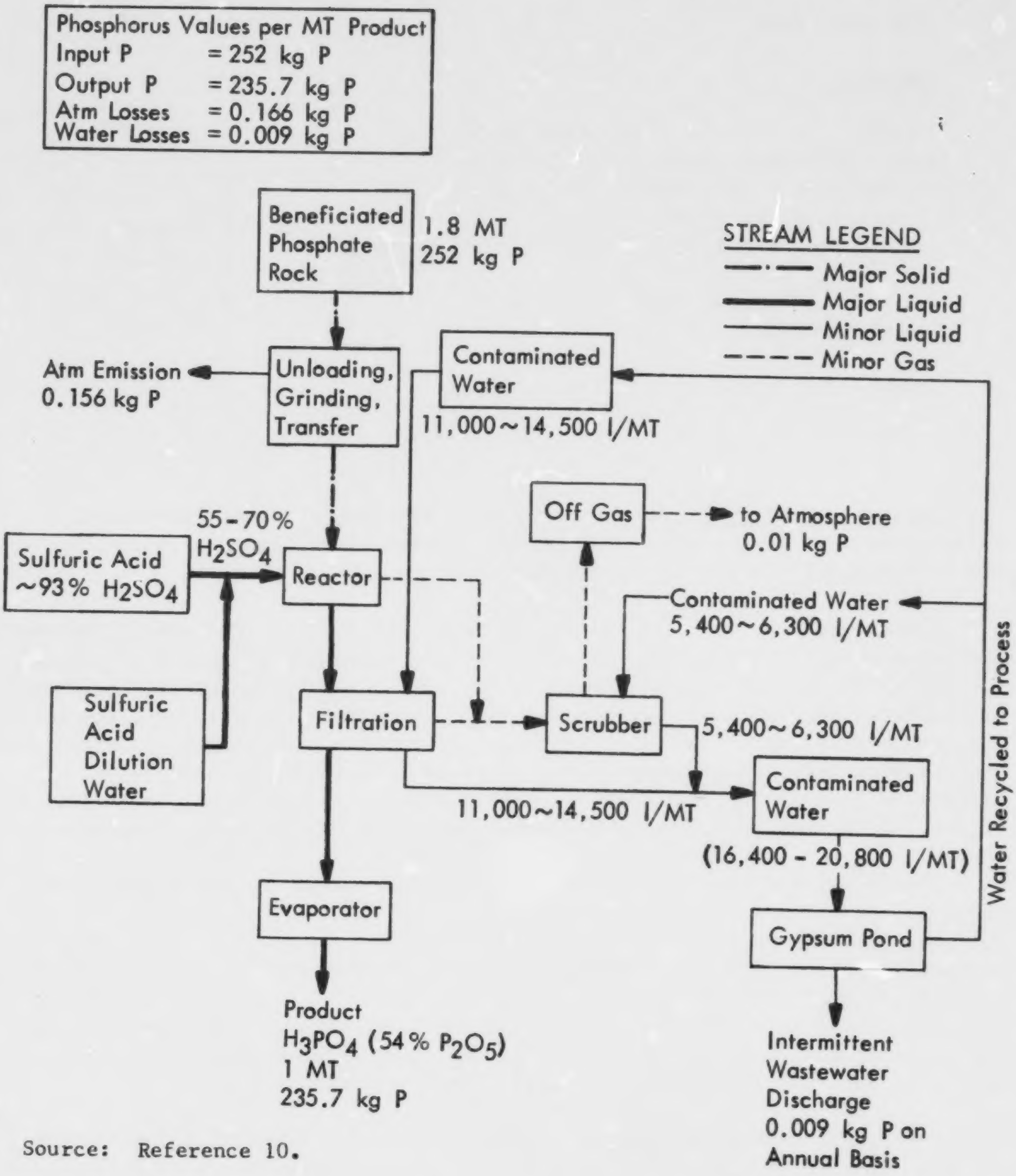
Wet Process Phosphoric Acid Production (SIC No. 2874)--

The manufacturing process (dihydrate process), shown in a representative flowsheet in Figure 6-3, is the sole source of fertilizer phosphoric acid in the United States. This acid is used as a raw material in the production of triple superphosphates and ammonium phosphate fertilizers. Aqueous sulfuric acid is reacted with ground phosphate rock to convert the tricalcium phosphate to orthophosphoric acid as shown in the following reaction.[10,11]

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \longrightarrow 10CaSO_4 \cdot 2H_2O + 6H_3PO_4 + 2HF\uparrow$$

Insoluble calcium sulfate dihydrate (gypsum) and hydrofluoric acid are also produced. The gypsum is separated from the acid and discharged to a pond, which also serves as a recycle water basin. Most of the released HF is recovered in an exhaust gas scrubber. The weak phosphoric acid is concentrated in an evaporator to yield a product containing about 54% P_2O_5. Detailed descriptions of this process are given in the literature.[10,11]

Material balance data[12]--The material requirements on the basis of 1 MT of phosphoric acid (54% P_2O_5 or 75% H_3PO_4) plus about 3 MT of waste gypsum are: beneficiated phosphate rock (14% phosphorus), 1.8 MT (0.252 MT phosphorus); and sulfuric acid (94%), 1.7 MT. Overall yield of H_3PO_4 based on phosphorus content of raw material is 95%. A phosphorus mass balance showing values which apply for 1 MT of phosphoric acid product follows:


Phosphorus Values per MT Product
Input P = 252 kg P
Output P = 235.7 kg P
Atm Losses = 0.166 kg P
Water Losses = 0.009 kg P
Beneficiated Phosphate Rock
1.8 MT
252 kg P
STREAM LEGEND
Major Solid
Major Liquid
Minor Liquid
Minor Gas
Atm Emission
0.156 kg P
Unloading, Grinding, Transfer
Contaminated Water
11,000~14,500 l/MT
Off Gas
to Atmosphere
0.01 kg P
55-70%
H_2SO_4
Sulfuric Acid
~93% H_2SO_4
Reactor
Contaminated Water
5,400~6,300 l/MT
Sulfuric Acid Dilution Water
Filtration
Scrubber
5,400~6,300 l/MT
Contaminated Water
11,000~14,500 l/MT
(16,400 - 20,800 l/MT)
Water Recycled to Process
Evaporator
Gypsum Pond
Product
H_3PO_4 (54% P_2O_5)
1 MT
235.7 kg P
Intermittent Wastewater Discharge
0.009 kg P on Annual Basis

Source: Reference 10.

Figure 6-3. Flow diagram for production of wet-process phosphoric acid.

Input			
Phosphate rock	252 kg P		
Outputs			
Product	235.7 kg P		
Total wastewater losses	0.009 kg P		Total P losses, 0.175 kg
Atmospheric losses from unloading, grinding, and transferring P rock	0.156 kg P	Total atm. losses, 0.166 kg P	
Atmospheric losses from wet scrubber	0.01 kg P		
Unaccounted for P	16.125 kg P		

Wastewater effluent--The three types of wastewater streams generated at wet-process acid plants are: (a) contact process water, (b) noncontact cooling water, and (c) steam condensate.13/

Contact process water is defined as water which comes into direct contact with process materials during the manufacturing operations. Sources of contact process wastewater include scrubber liquor, gypsum slurry, barometric condensers (for reactor) and acid sludge. Recycled gypsum pond water is utilized in the scrubber system to remove particulates, fluorides, and phosphates from the gas streams. This contact wastewater, combined with the steam condensate, contains varying quantities of phosphoric acid along with fluorides, sulfates and gypsum.13/ The insoluble gypsum particles contain a small amount of phosphorus.

Data which define the extent of wastewater disposal or containment practices in the domestic phosphate fertilizer industry have been reported in the literature.10/ As shown in Table 6-7 (page 110), only about 12% of all domestic wet-process plants discharge wastewater to the environment, and two-thirds of these facilities add lime to remove phosphorus prior to discharge. Facilities with no wastewater discharge contain their effluent in specially designed gypsum ponds or abandoned phosphate rock mining pits. At some plants, scrubber liquor is sold for fertilizer or fluorine recovery.13/

The permissable phosphorus concentrations in this effluent under the EPA effluent limitation guidelines for best practicable technology currently available (BPCTCA) is a maximum average discharge for 10 or more consecutive days of 35 mg of total phosphorus per liter.10/ This discharge value was used in estimating the total phosphorus discharge in effluent from wet-process acid plants.

As shown in Figure 6-3, the contaminated water input to the gypsum pond ranges from 16,400 liters/MT P_2O_5 to 20,800 liters/MT of P_2O_5 in the product. Assuming the average flow is 18,600 liters/MT of P_2O_5 in product, the annual phosphorus discharge from the gypsum pond can be estimated to be 0.0088 kg phosphorus per metric ton of phosphoric acid.

It was assumed that for those plants which discharge effluent, the total discharge period each year is 2.5 months (Martin, W., Personal Communication, EPA, Effluent Guidelines Division, Washington, D.C., January 1978).

Atmospheric emissions--Dust losses to the atmosphere occur during the handling and grinding of phosphate rock. The dust particles contain phosphorus in the form of tricalcium phosphate.

Off-gases containing some phosphoric acid mist and other particulate emissions are treated in a wet-scrubber as a means of reducing air emissions. Most of the phosphorus in the gas stream is removed in this scrubber unit and transferred to a wastewater stream. Recycled gypsum pond water is used in the wet-scrubber system.

Particulate emissions from the reactor are comprised of unreacted phosphate rock, and lesser amounts of insoluble salts and gypsum. These particles are entrained in reactor gases vented to the wet scrubber. About 80% of the particulate matter consists of water-soluble phosphorus compounds.[13/]

Estimates relating to total phosphorus air emissions in the wet process for production of phosphoric acid are summarized in Table 6-4. The estimating procedures are described below; the estimated emissions apply for 1 MT of product (wet process phosphoric acid).

Grinding of phosphate rock--The uncontrolled particulate emission is 10 kg/MT of product. The P_2O_5 content in the emission is 32% and the level of emission control is 97%.[5/] From this, estimated phosphorus emission is 0.04 kg phosphorus per metric ton product.

Material handling--For unloading phosphate rock, the average controlled emission factor is 0.15 g particulate per kilogram of P_2O_5 in product.[13/] The rock contains 32% P_2O_5. One metric ton of product acid contains 540 kg of P_2O_5. Then, the estimated phosphorus emission is 0.113 kg phosphorus per metric ton product.

For phosphate rock transfer and conveying, the reported controlled emission factor is 0.045 g particulate per kilogram of P_2O_5 in product.[13/] The estimated phosphorus emission is 0.003 kg phosphorus per metric ton product.

TABLE 6-4. SOURCES AND ESTIMATES OF PHOSPHORUS-CONTAINING AIR EMISSIONS FOR WET PROCESS PHOSPHORIC ACID PRODUCTION

Production activity	Uncontrolled particulate emission factor (kg/MT product)	Controlled emission factor		% P_2O_5 in emissions	Total P emissions after controls (kg P/MT product)
		Grams of particulate/MT of P_2O_5 in product	Grams of P_2O_5 per MT of P_2O_5 in product		
Grinding phosphate rock	10	NA	NA	32	0.040
Material handling:					
Phosphate rock unloading	NA	0.15	NA	32	0.113
Phosphate rock transfer and conveying	NA	0.045	NA	32	0.003
Wet scrubber system	NA	NA	0.038	NA	0.01
Total					0.166

Source: References 5 and 13.

NA = Not available.

The total estimated phosphorus emission caused by material handling is approximately 0.12 kg phosphorus per metric ton product.

Wet scrubber system--The reported average overall controlled emission factor for this system is 0.038 g of P_2O_5 per kilogram of P_2O_5 in product.13/ The estimated phosphorus emission is approximately 0.01 kg phosphorus per metric ton product.

National emission for wet-process phosphoric acid production--The estimated wastewater emission factor is 0.0088 kg phosphorus per metric ton and the estimated production level in 1978 is 6,600,000 MT (Table 6-17); the emission is estimated to be 58 MT phosphorus.

The air emission factor is 0.166 kg phosphorus per metric ton. Thus, the total air emission is calculated to be 1,095 MT phosphorus.

Superphosphoric Acid Production (SIC No. 2874)--

When orthophosphoric acid (54% P_2O_5), produced by the wet-process, is heated at elevated temperatures a molecular dehydration occurs and polyphosphoric acid chains are formed. For example, tripolyphosphoric acid can be prepared as follows:13/

$$3H_3PO_4 \longrightarrow H_5P_3O_{10} + 2H_2O$$

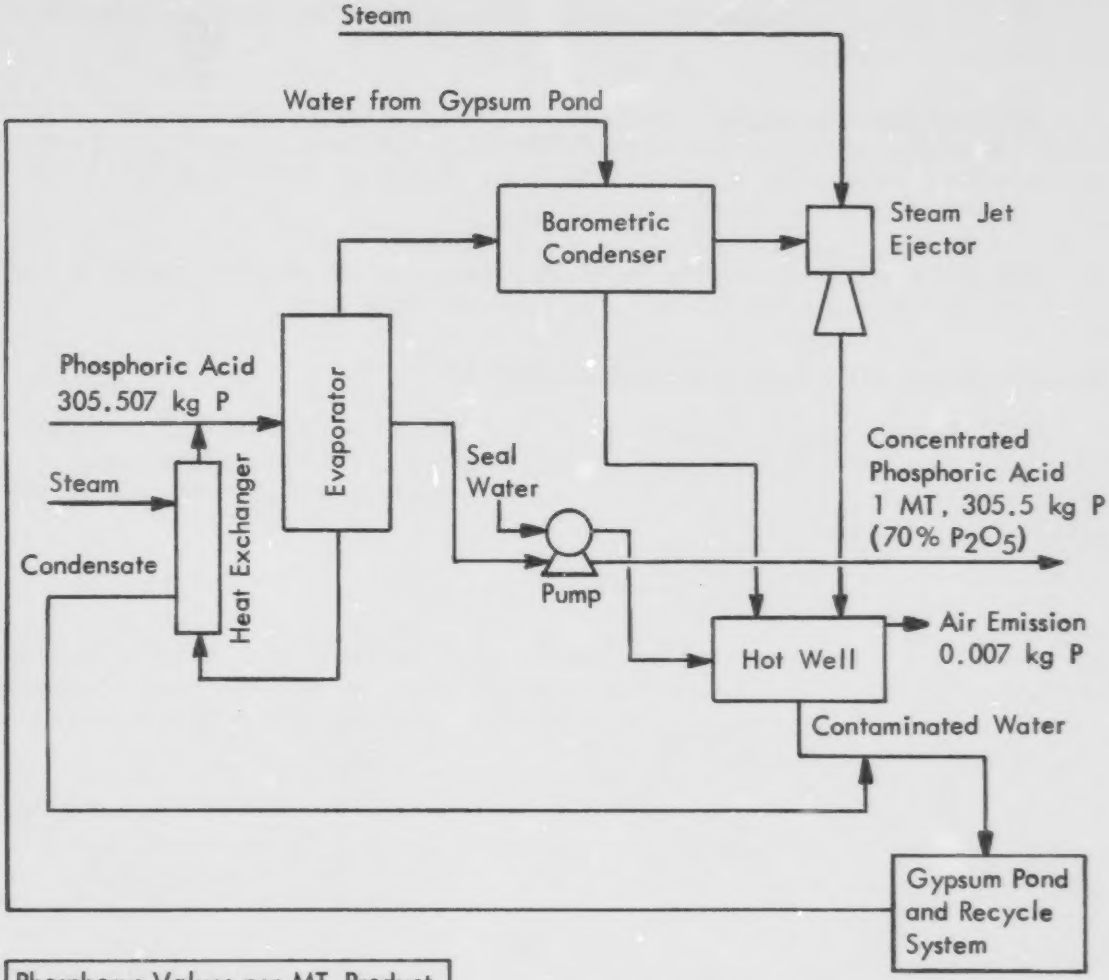
The product, a mixture of orthophosphoric acid and dehydrated acids of differing chain lengths, is called superphosphoric acid. Wet process superphosphoric acid is concentrated to 68.5 to 72% P_2O_5.13/ A representative process flow diagram is shown in Figure 6-4.

The commercial processes used in the United States are (a) submerged combustion and (b) vacuum evaporation. About 75% of the existing domestic plants use the latter process.13/ Superphosphoric acid is used in the preparation of high analysis phosphate fertilizers.

Mass balance data--A phosphorus mass balance showing values which apply for 1 MT of product superphosphoric acid follows:

Input P	305.507 kg P	
Output in product	305.5 kg P	
Atmospheric losses	0.007 kg P	Total P losses, 0.007 kg
Wastewater losses	0 kg P	

Wastewater effluent--Wastewater streams are discharged from barometric condensers, steam-jet ejectors, and wet scrubbers in superphosphoric acid plants. These streams contain orthophosphoric acid and fluorides.13/


Steam
Water from Gypsum Pond
Barometric Condenser
Steam Jet Ejector
Phosphoric Acid
305.507 kg P
Evaporator
Steam
Heat Exchanger
Condensate
Seal Water
Pump
Concentrated Phosphoric Acid
1 MT, 305.5 kg P
(70% P_2O_5)
Air Emission
0.007 kg P
Hot Well
Contaminated Water
Gypsum Pond and Recycle System

Phosphorus Values per MT Product
Input P = 305.507 kg P
Output P = 305.5 kg P
Atm Losses = 0.007 kg P
Water Losses = 0 kg P

Source: Reference 13.

Figure 6-4. Flow diagram for production of superphosphoric acid.

Data in Table 6-7 indicate that none of superphosphoric acid plants discharge wastewater.

Atmospheric emissions--Emission species include fluoride compounds and particulates. Particulates are limited to liquid phosphoric acid, aerosols, and mists. One plant has reported particulate emissions ranging from 0.011 to 0.055 g/kg P_2O_5.13/ The estimated phosphorus emission, based on these data, is 0.01 g phosphorus per kilogram P_2O_5 in product. If it is assumed that the product contains 70% P_2O_5, then the estimated phosphorus emission (per metric ton of superphosphoric acid) is 0.007 kg phosphorus.

National emission for superphosphoric acid production--No wastewater is discharged from this production process.13/

Based on emission factors and production data shown in Table 6-4 the national air emission can be estimated to be 4 MT phosphorus.

Normal Superphosphate Production (SIC No. 2874)--

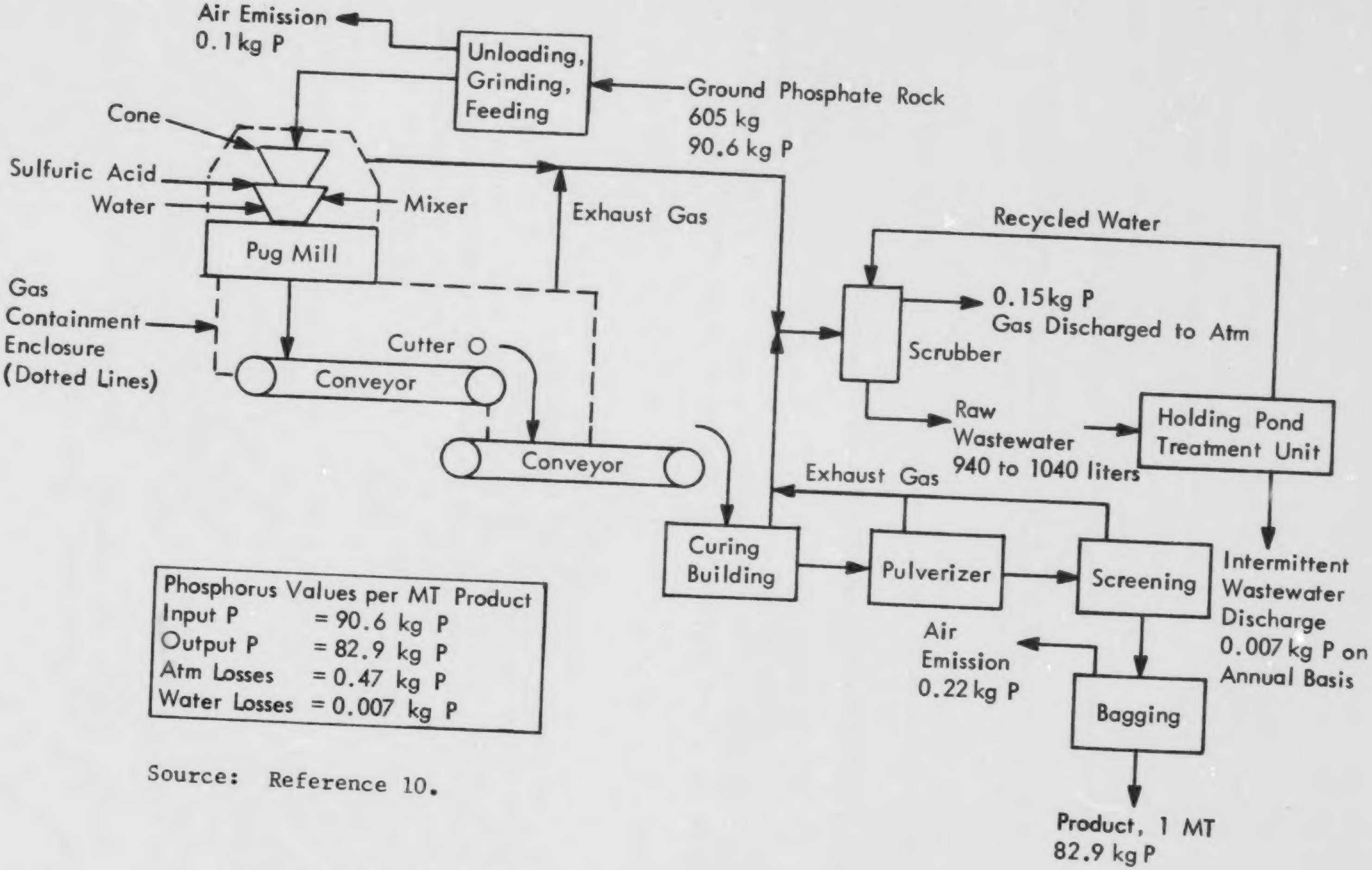
A representative flowsheet for the domestic production of normal superphosphate (NSP) is given in Figure 6-5. The production of NSP basically involves the reaction of ground phosphate rock with sulfuric acid to form monocalcium phosphate according to the overall reaction:10/

$$Ca_{10}(PO_4)_6F_2 + 7H_2SO_4 + 17H_2O \longrightarrow 7CaSO_4 \cdot 2H_2O + 3Ca(H_2PO_4)_2 \cdot H_2O + 2HF\uparrow$$

The process involves four steps: (a) preparation of phosphate rock; (b) mixing of phosphate rock with sulfuric acid; (c) curing and drying of the original slurry by completion of the reactions; and (d) excavation, milling, screening, and bagging of the finished NSP product. During the processing operations, no attempt is made to separate the calcium sulfate from the monocalcium phosphate. Thus, the presence of the calcium sulfate results in a relatively impure fertilizer product. Detailed descriptions of this process are given in the literature.10,11/

Material balance data--The weight ratio of phosphate rock to finished NSP product is 0.605:1 when the feed material contains 34.3% P_2O_5 (or 14.98% phosphorus).11/ On this basis, 1 MT of product is equivalent to 0.605 MT (605 kg) of phosphate rock. It was assumed that the average P_2O_5 content in the product is 19% (or 8.29% phosphorus).11/ Then, the product shown on the flowsheet contains 82.9 kg phosphorus and the phosphate rock contains 90.6 kg phosphorus.

A phosphorus mass balance showing values which apply for 1 MT of product normal superphosphate is as follows:


Air Emission
0.1 kg P
Unloading, Grinding, Feeding
Ground Phosphate Rock
605 kg
90.6 kg P
Cone
Sulfuric Acid
Water
Mixer
Pug Mill
Exhaust Gas
Gas Containment Enclosure (Dotted Lines)
Cutter
Conveyor
Conveyor
Recycled Water
0.15 kg P
Gas Discharged to Atm
Scrubber
Raw Wastewater
940 to 1040 liters
Holding Pond Treatment Unit
Exhaust Gas
Curing Building
Pulverizer
Screening
Intermittent Wastewater Discharge
0.007 kg P on Annual Basis
Air Emission
0.22 kg P
Bagging
Product, 1 MT
82.9 kg P
Phosphorus Values per MT Product
Input P = 90.6 kg P
Output P = 82.9 kg P
Atm Losses = 0.47 kg P
Water Losses = 0.007 kg P

Source: Reference 10.

Figure 6-5. Flow diagram for production of normal superphosphate.

Input P	90.6 kg P		

Outputs

Product	82.9 kg P		
Wastewater discharge	0.007 kg P		
Atmospheric losses from unloading, grinding, and feeding P ore	0.1 kg P	Total water effluent losses, 0.007 kg P Total atm. losses, 0.47 kg P	Total P losses, 0.477 kg
Atmospheric losses from wet scrubber	0.15 kg P		
Atmospheric losses from bagging	0.22 kg P		
Unaccounted for P	7.22 kg P		

Wastewater effluent--Current information on the wastewater containment practices and the extent of wastewater disposal in the phosphate fertilizer industry has been described. Inquiries reportedly made to 80% of the domestic NSP fertilizer plants have shown that only 4% discharge wastewater (see Table 6-7).[13] This survey indicated that practically all of the discharging plants treat their wastewater with lime to remove most of the contained phosphorus, before discharging the effluent to surface waters. On the basis of this information, it was assumed in this study that a holding and treatment pond is provided for each fertilizer plant operation and that wastewater is impounded and recirculated in the plant. Also, it was assumed that the phosphorus content in the treated effluent from NSP plants corresponds to the EPA effluent limitation guidelines for best practical control technology currently available (i.e., a maximum average discharge for 10 or more consecutive days of 35 mg total phosphorus per liter of wastewater).[10] It was further assumed that for those plants which discharge effluent, the total discharge period each year would be 2.5 months.

The range of discharge rates of contaminated wastewater from the wet scrubber is 940 to 1,040 liters/MT of NSP product.[10] Assuming an average flow rate of 990 liters/MT, the estimated discharge of phosphorus in wastewater to the environment is calculated to be 0.035 kg total phosphorus per metric ton product. For a 2.5-month period of discharge each year, the annual phosphorus release in wastewater would be 0.007 kg/MT of NSP.

Atmospheric emissions--In NSP production plants, the air emission points (see Figure 6-5) are the ore grinding operation, the mixer, conveying equipment, the curing building, materials handling, product pulverizing, and bagging.[14]

The particles emitted from NSP processing range from finely divided rock phosphate to finished fertilizer.[5] Phosphate rock particles tend to be large, and therefore, usually settle near the emission point. Phosphate rock particles contain tricalcium phosphate in concentrations from 15 to 80% equivalent weight of P_2O_5. This phosphate is stable and essentially insoluble in water.

Estimates of the phosphorus losses from atmospheric releases to the environment during NSP production were based on information contained in References 5 and 14. Data developed in these estimates are tabulated in Table 6-5. The estimating procedures used are described below; all estimates are based on 1 MT of NSP product.

Grinding of phosphate rock--The uncontrolled particulate emission is reported to be 3 kg/MT of product.[5] The particulate contains 34% P_2O_5, the level of emission control is 80%, and the emission is calculated to be 0.09 kg phosphorus per metric ton product.

Material handling--The average controlled emission factor for unloading phosphate rock is 0.28 g of particulate per kilogram of P_2O_5 in product.[14] The phosphate rock contains 34% P_2O_5 and the product contains 19% P_2O_5. The estimated phosphorus emission is 0.008 kg phosphorus per metric ton product.

For phosphate rock feeding, the controlled emission is reported to be 0.055 g of particulate per kilogram of P_2O_5 in product.[14] The estimated phosphorus emission is 0.0016 kg phosphorus per metric ton product.

Mixer and den--A reported controlled emission factor for this source is 0.26 g of particulate per kilogram of P_2O_5 in product.[14] The estimated phosphorus emission is 0.004 kg phosphorus per metric ton product.

Curing building--The controlled emission factor is 3.6 g of particulate per kilogram of P_2O_5 in product.[14] The estimated phosphorus emission is 0.057 kg phosphorus per metric ton product.

Product grinding--The uncontrolled particulate emission factor is 0.25 kg of P_2O_5 per metric ton product,[5] and the level of emission control is 80%. The phosphorus emission is estimated to be 0.02 kg phosphorus per metric ton product.

Product screening--The estimated uncontrolled emission factor is 1 kg of particulate per metric ton of product and the level of emission control is 85%.[5] The emission is estimated at 0.07 kg phosphorus per metric ton product.

TABLE 6-5. SOURCES AND ESTIMATES OF PHOSPHORUS-CONTAINING AIR EMISSIONS FOR NORMAL SUPERPHOSPHATE PRODUCTION

Production activity	Uncontrolled particulate emission factor (kg/MT product)	Controlled emission factor (g of particulate per 1 MT P_2O_5 in product)	Estimated level of emission control (%)	% P_2O_5 in emissions	Total P emissions after controls (kg P/MT product)
Grinding phosphate rock	3	NA	80	34	0.090
Material handling:					
Phosphate rock unloading	NA	0.28	NA	34	0.008
Phosphate rock feeding	NA	0.055	NA	34	0.002
Mixer and den	NA	0.26	NA	19	0.004
Curing building	NA	3.6	NA	19	0.057
Product grinding	0.25	NA	80	a/	0.02
Product screening	1	NA	85	a/	0.07
Product bagging or bulk loading	0.5b/	NA	b/	a/	0.22
Total					0.47

Sources: References 5 and 14.

a/ Emission factor includes % P_2O_5.

b/ Emission factor after control.

NA - Not available.

Product bagging or bulk loading--The reported controlled emission factor is 0.5 kg P_2O_5 per metric ton product.[5] The estimated emission is 0.22 kg phosphorus per metric ton product.

National emission for NSP production--About 4% of the domestic producers discharge wastewater.[13]

The annual wastewater emission based on the estimated emission factor (0.0007 kg phosphorus per metric ton product) and the 1978 production rate (390,000 MT) shown in Table 6-17 can be calculated to be < 0.1 MT phosphorus.

Based on the tabulated data shown in Table 6-16, the estimated annual phosphorus discharge in air emissions can be calculated at 183 MT phosphorus.

Triple Superphosphate Production (SIC No. 2874)--

The two principal types of commercial triple superphosphate (TSP) are granular (GTSP) and run-of-the-pile grade (ROP-TSP). The processing conditions and physical characteristics differ significantly for these two products. The GTSP product is a hard, uniform, pelletized granule whereas the ROP-TSP product is a nonuniform pulverized mass. The GTSP process accounts for about 60% of total TSP production, and the ROP process is used for the remaining 40%.[14]

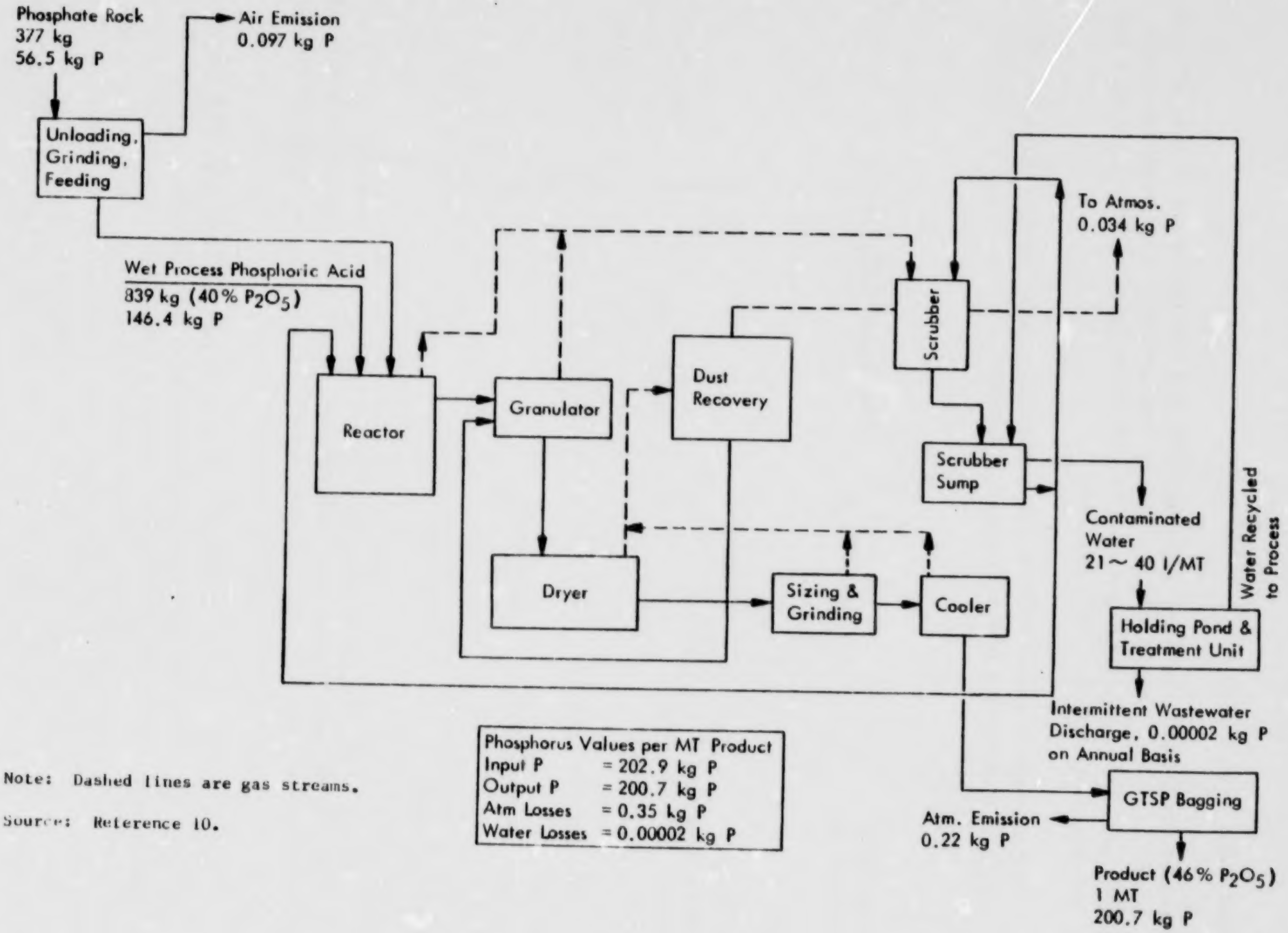
Both processes use the same raw materials, ground phosphate rock and wet-process phosphoric acid. The basic chemical reaction is:

$$Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 + 10H_2O \longrightarrow 10Ca(H_2PO_4)_2 \cdot H_2O + 2HF$$

The similarity between the two processes ends at this point. For a detailed description of the technology for these processes the reader is referred to References 10 and 11. An analysis and discussion of each process follows.

The GTSP process--Figure 6-6 presents a representative flow diagram for this process. A relatively low strength (40% P_2O_5) phosphoric acid is used in the reaction with phosphate rock. The low strength acid maintains the resultant slurry in a fluid state and permits the chemical reaction to proceed further toward completion before it solidifies. This slurry is transferred to a granulator which produces pelletized material. These pellets are dried, sized, cooled and bagged as final product. In some cases, ROP-TSP is granulated to form GTSP; however, less than 10% of the total GTSP consumed domestically is produced by this method.[14]

Material balance data--On the basis of data from the literature, the following material balance for TSP was developed.[15]


Phosphate Rock
377 kg
56.5 kg P
Air Emission
0.097 kg P
Unloading, Grinding, Feeding
Wet Process Phosphoric Acid
839 kg (40% P2O5)
146.4 kg P
Reactor
Granulator
Dryer
Dust Recovery
Sizing & Grinding
Cooler
Scrubber
Scrubber Sump
To Atmos.
0.034 kg P
Contaminated Water
21 ~ 40 l/MT
Water Recycled to Process
Holding Pond & Treatment Unit
Intermittent Wastewater Discharge, 0.00002 kg P on Annual Basis
GTSP Bagging
Atm. Emission
0.22 kg P
Product (46% P2O5)
1 MT
200.7 kg P
Phosphorus Values per MT Product
Input P = 202.9 kg P
Output P = 200.7 kg P
Atm Losses = 0.35 kg P
Water Losses = 0.00002 kg P

Note: Dashed lines are gas streams.

Source: Reference 10.

Figure 6-6. Flow diagram for production of granulated triple superphosphate.

Raw material	Kilogram	Product	Kilogram
Phosphate rock (34% P_2O_5)	420	GTSP (46% P_2O_5)	1,000
Phosphoric acid (40% P_2O_5)	815		

The phosphate rock contains 14.84% phosphorus and the phosphoric acid contains 17.46% phosphorus. The amount of phosphorus contained in the phosphate rock is 62.3 kg, and the phosphorus present in the phosphoric acid is 142 kg. The product TSP contains 200.7 kg phosphorus.

A phosphorus mass balance showing values which apply for 1 MT of granulated triple superphosphate product follows:

Inputs

Phosphate rock	56.5 kg P	Total input 202.9 kg P
Phosphoric acid	146.4 kg P	

Outputs

Product GTSP	200.7 kg P		Total accounted for P losses, 0.351 kg
Wastewater discharge	0.00002 kg P		
Atmospheric losses from unloading, grinding, and feed P rock	0.097 kg P	Total atm. losses, 0.35 kg P	
Atmospheric losses from scrubber	0.034 kg P		
Atmospheric losses from bagging	0.22 kg P		
Unaccounted for P	1.85 kg P		

Wastewater effluent--The data in Table 6-7 show that only 10% of the domestic TSP plants discharged any wastewater to the environment in 1977. These data also indicate that all discharging plants treat the contaminated wastewater with lime to reduce the phosphorus level.

The data in Figure 6-6 show that the input of contaminated water to a holding pond ranges from 21 to 40 liters/MT product. The EPA effluent limitations guidelines for best practicable control technology currently available (BPCTCA) specify that the maximum average concentration in this wastewater, when discharged, shall be 35 mg phosphorus per liter.[10] It was assumed that due to adverse weather conditions, 10% of the plants (see Table 6-7) discharged treated effluent at 35 mg phosphorus per liter for a total of 2.5 months each year at a discharge rate of 30 liters/MT product. On an annual basis, the estimated amount of phosphorus in discharged wastewater is 0.00002 kg phosphorus per metric ton product.

Atmospheric emissions--In the GTSP manufacturing process the operating areas contributing to losses of phosphorus to the atmosphere include particulate emissions from rock unloading, pulverizing and feeding, reaction/granulation, drying/cooling, grinding/screening, and bagging.[14] These particulates are phosphate rock or fertilizer.

The atmospheric emissions of phosphorus from the processes are estimated on the basis of data reported in the literature.[5,14] The estimation procedure is similar to that described on page 98. The results are shown in Table 6-6. The estimated total air emissions are 0.35 kg of total phosphorus per metric ton product.

The ROP-TSP process--A flow diagram representative of this process is presented in Figure 6-7. The method is very similar to the NSP process with the exception that phosphoric acid rather than sulfuric acid is used as the acidulating medium. The mixing of acid (46 to 54% P_2O_5) and rock is normally conducted in a cone mixer. After discharge from the mixer, the slurry quickly (15 to 30 sec) becomes plastic. Solidification, with evolution of gas, occurs on a slowly moving conveyor (den) enroute to a curing area, where the product remains for 2 to 4 weeks. Following curing, the ROP-TSP material is sized and shipped in bulk.

Material balance data--The estimated raw material and product quantities are as follows:[16]

Raw materials	Kilogram	Product	Kilogram
Phosphate rock (34% P_2O_5)	420	ROP-TSP (46% P_2O_5)	1,000
Phosphoric acid (50% P_2O_5)	652		

The quantity of phosphorus present in the phosphate rock is 62.3 kg and the quantity of phosphorus in the phosphoric acid is 142.3 kg. The product (ROP-TSP) contains 200.7 kg phosphorus.

A phosphorus mass balance showing values which apply for 1 MT of product (ROPOTSP) follows:

TABLE 6-6. SOURCES AND ESTIMATES OF PHOSPHORUS-CONTAINING AIR EMISSIONS FOR TRIPLE SUPERPHOSPHATE PRODUCTION

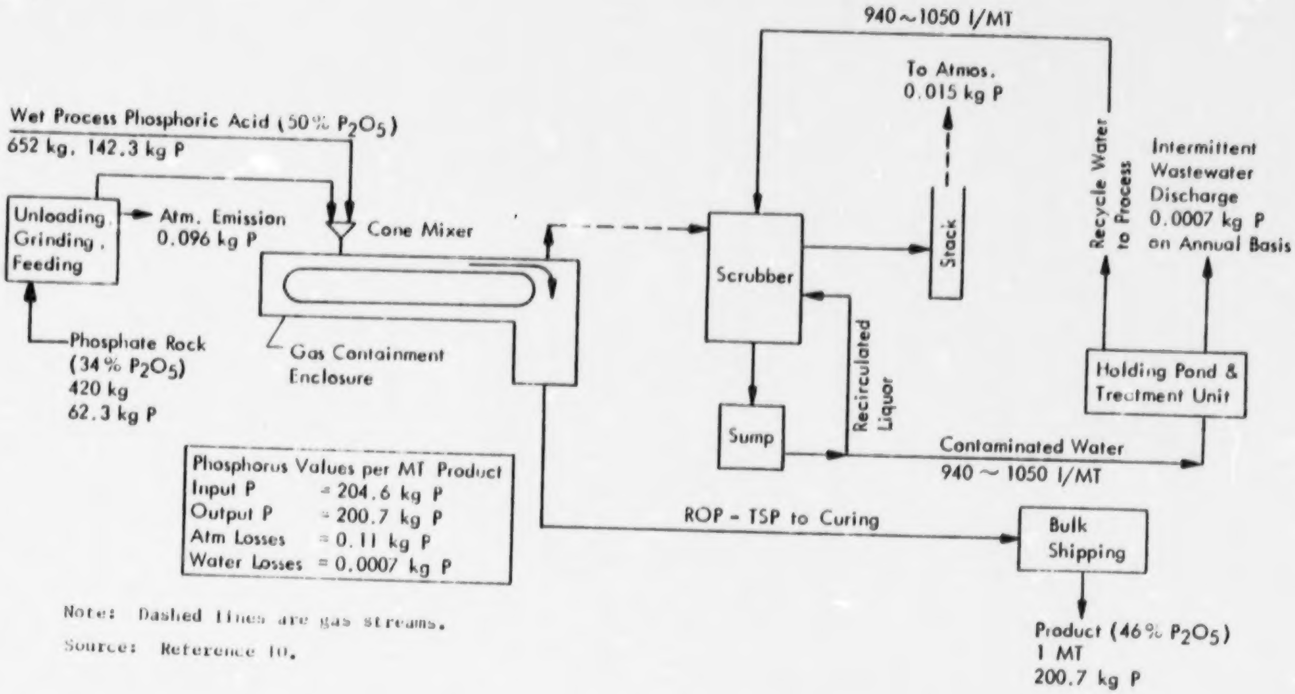
Production activity	Uncontrolled particulate emission factor (kg/MT product)	Controlled emission factor (g of particulate per 1 MT P_2O_5 in product)	P_2O_5 in emissions (%)	Estimated level of emission control (%)	Total P emission after controls (kg P/MT product)
GTSP Process					
Rock unloading	NA	0.09	34	NA	0.006
Rock grinding	3	NA	34	80	0.090
Rock feeding	NA	0.017	34	NA	0.001
Reactor, granulator, dryer, cooler, screens	NA	0.05	46	NA	0.0045
Cooling building	NA	0.10	46	NA	0.009
Product grinding	0.25	NA	a/	80	0.02
Product bagging	0.5	NA	a/	NA	0.22
Total					0.35
ROP-TSP process					
Rock unloading	NA	0.07	34	NA	0.005
Rock grinding	3	NA	34	80	0.090
Rock feeding	NA	0.014	34	NA	0.001
Cone mixer, den, curing building	NA	0.16	46	NA	0.015
Total					0.11

Sources: References 5 and 14.

a/ Emission factor includes % P_2O_5.

b/ Emission factor after control.

NA = Not available.


Wet Process Phosphoric Acid (50% P_2O_5)
652 kg, 142.3 kg P
Unloading, Grinding, Feeding
Atm. Emission
0.096 kg P
Cone Mixer
Phosphate Rock
(34% P_2O_5)
420 kg
62.3 kg P
Gas Containment Enclosure
Phosphorus Values per MT Product
Input P = 204.6 kg P
Output P = 200.7 kg P
Atm Losses = 0.11 kg P
Water Losses = 0.0007 kg P
940 ~ 1050 l/MT
To Atmos.
0.015 kg P
Scrubber
Stack
Sump
Recirculated Liquor
Contaminated Water
940 ~ 1050 l/MT
Recycle Water to Process
Intermittent Wastewater Discharge
0.0007 kg P
on Annual Basis
Holding Pond & Treatment Unit
ROP - TSP to Curing
Bulk Shipping
Product (46% P_2O_5)
1 MT
200.7 kg P

Note: Dashed lines are gas streams.

Source: Reference 10.

Figure 6-7. Flow diagram for production of run-of-pile triple superphosphate.

Inputs

Phosphate rock	62.3 kg P	Total input, 204.6 kg P
Phosphoric acid	142.3 kg P	

Outputs

Product, ROP-TSP	200.7 kg P		
Wastewater discharge	0.0007 kg P		Total P losses, 0.1117 kg
Atmospheric losses from unloading, grinding, and feeding of P rock	0.096 kg P	Total atm. losses, 0.111 kg P	
Atmospheric losses from scrubber vent	0.015 kg P		

Unaccounted for P	3.79 kg P

Wastewater effluent--The wastewater treatment and management procedure is identical to that discussed for the GTSP process. The input of contaminated water to the holding pond ranges from 940 to 1,050 liters/MT product;[10] an average rate of 1,000 liters/MT product was assumed. This leads to an annual phosphorus release in wastewater of 0.0007 kg phosphorus per metric ton product.

Atmospheric emissions--The emission sources and waste components are similar to those described for the NSP plant. The emissions of particulates and fluoride vapors from the cone mixer, conveyor chamber, and curing building are controlled by wet scrubbers using recirculated pond water. Particulate emissions from rock grinding, storage, and transfer facilities are controlled by baghouse filters.[14]

The air emissions of phosphorus from the ROP process were estimated on the basis of published information.[5] The estimation procedure was identical to that described on page 98 and the results are summarized in Table 6-6. The estimated total air emissions are 0.11 kg phosphorus per metric ton of TSP product.

National emission for TSP production--For TSP 60% of total production is by the GTSP process while 40% is by the ROP process.[14] About 10% of the domestic producers discharge wastewater (treated) to the environment (see Table 6-7).[13] Using the appropriate 1978 production data and emission data shown in Table 6-17, the annual total quantity of phosphorus released in wastewater is approximately 0.5 MT. For air emissions, the annual total quantity is about 334 MT phosphorus for the GTSP process and 70 MT for the ROP-TSP process.

Production of Ammonium Phosphates (SIC No. 2874)--

Ammonium phosphates are normally prepared by the neutralization of orthophosphoric acid with ammonia. The product obtained depends on the ratio of phosphoric acid and ammonia used, and may be monoammonium phosphate ($NH_4H_2PO_4$) (MAP), diammonium phosphate [$(NH_4)_2HPO_4$] (DAP), or a mixture of the two. Although these products can be made from either furnace or wet-process acid, all products currently intended for fertilizer use are based on wet-process acid.

A representative flow diagram for production of DAP is presented in Figure 6-8. The processing method and phosphorus releases for MAP, the other major product of this type, are very similar. Thus, the data developed for phosphorus emissions apply generally for all ammonium phosphate processes.

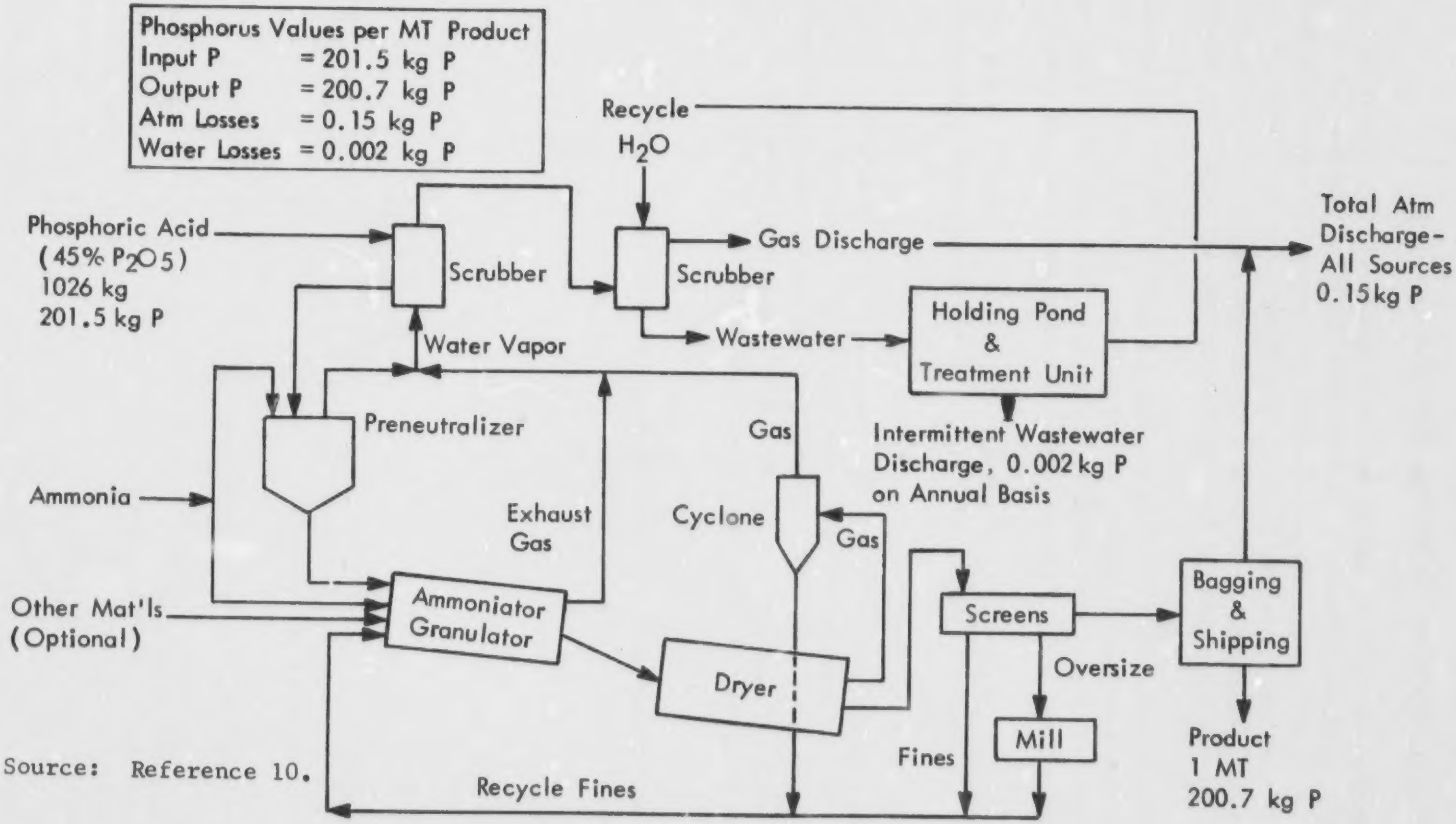
Material balance data--For purposes of calculation, a DAP production composition of 18-46-0 (18% N, 46% P_2O_5, 0% K_2O), a common commercial grade was used.

The production of 907 kg (1 short ton) of this product requires 418.6 kg of P_2O_5 in the form of phosphoric acid.[11] The quantity of phosphoric acid (45% P_2O_5) required is 930.2 kg and the amount of ammonia required is 197.7 kg. On the basis of the production of 1 MT of DAP, the quantity of phosphoric acid required is 1,026 kg. The phosphorus contained in this quantity of acid is 201.5 kg.

A phosphorus mass balance showing values which apply for 1 MT of product ammonium phosphate is as follows:

Input		
Phosphoric acid	201.5 kg P	
Output		
Product	200.7 kg P	
Total wastewater discharge	0.002 kg P	Total P losses, 0.152 kg
Total atmospheric losses	0.15 kg P	
Unaccounted for P	0.648 P	

Wastewater effluent--The allowable phosphorus concentration in wastewater discharged to environment from this process according to the EPA effluent limitations guidelines for best practicable control technology currently available (BPCTCA) is a maximum average discharge for 10 or more consecutive days of 35 mg of total phosphorus per liter.[10] This value was used to estimate the total phosphorus discharge in effluent from ammonium phosphate plants.


Phosphorus Values per MT Product
Input P = 201.5 kg P
Output P = 200.7 kg P
Atm Losses = 0.15 kg P
Water Losses = 0.002 kg P
Phosphoric Acid
(45% P_2O_5)
1026 kg
201.5 kg P
Ammonia
Other Mat'ls
(Optional)
Scrubber
Water Vapor
Preneutralizer
Recycle
H_2O
Scrubber
Gas Discharge
Wastewater
Exhaust
Gas
Ammoniator
Granulator
Gas
Cyclone
Gas
Dryer
Holding Pond
&
Treatment Unit
Intermittent Wastewater
Discharge, 0.002 kg P
on Annual Basis
Total Atm
Discharge-
All Sources
0.15 kg P
Screens
Oversize
Mill
Fines
Recycle Fines
Bagging
&
Shipping
Product
1 MT
200.7 kg P

Source: Reference 10.

Figure 6-8. Flow diagram for production of ammonium phosphate.

Data[10] show that the discharge of contaminated water from the scrubber to the holding pond ranges from 0 to 300 liters/MT of product for MAP to 5,000 to 6,500 liters/MT of product DAP.[10] It was assumed that during periods of wastewater discharge to the environment (2.5 months/year) that the average effluent discharge rate is 3,000 liters/MT.

Data on wastewater discharge practices are presented in Table 6-7. About 9% of all ammonium phosphate plants discharge wastewater. The estimated total phosphorus discharge on an annual basis is 0.002 kg phosphorus per metric ton of ammonium phosphate product.

Atmospheric emissions--The production activities, which are sources of atmospheric emissions of phosphorus, include the ammoniator-granulator step, product drying and cooling, material handling and product sizing and bagging. The characteristics of these emission streams are very similar to those which apply for NSP production.

Basic data for the estimation of the phosphorus losses to the atmosphere during production of DAP were obtained from the literature.[17] The results of the estimates on atmospheric emissions for DAP production are shown in Table 6-8. The estimated total emission of phosphorus was 0.15 kg phosphorus per metric ton of ammonium phosphate product.

National emission for ammonium phosphate production--The estimated production rate in 1978 is 3,550,000 MT of P_2O_5 (Table 6-17). Assuming the average P_2O_5 content in these products is 46% (as in a typical DAP product), the estimated total production rate is 7,717,400 MT of ammonium phosphate.

The unit emission factor for wastewater is 0.002 kg phosphorus per metric ton product (Table 6-17). The approximate discharge of contained phosphorus in this effluent is calculated to be 15 MT phosphorus.

Using the air emission factor, shown in Table 6-17, the annual phosphorus discharge to the atmosphere is estimated to be 1,150 MT phosphorus.

Defluorinated Phosphate Rock Production (SIC No. 2048)--

This product is consumed principally in the preparation of animal feed supplements. Three general methods have been developed in the United States to defluorinate phosphate rock.[18]

1. Treatment of NSP at elevated temperatures to volatilize the residual fluorine.

2. Treatment of a mixture of phosphate rock and silica in an oil-fired shaft furnace to volatilize the fluorine and yield a fused tricalcium phosphate mass.

TABLE 6-7. WATER EFFLUENT DISPOSAL AND CONTAINMENT PRACTICES FOR THE PHOSPHATE FERTILIZER INDUSTRY

Process water discharged?	Industry, percent of plants specified					
	Wet process phosphoric acid plants	Super-phosphoric acid plants	Normal super-phosphate plants	Triple super-phosphate plants	Ammonium phosphate plants	Total phosphate fertilizer industry
Yes						
Intermittently or continuously	12	0	4	10	9	8
With treatment	8	0	4	10	9	7
Without treatment	4	0	0	0	0	1
No						
Discharged to gypsum ponds	64	63	48	63	56	56
Facilities have emergency, or continual treatment of ponds	42	50	7	47	26	27
Facilities have no emergency treatment capabilities	11	13	7	0	13	8
Insufficient information	11	0	34	16	17	21
Process water discharged to abandoned mining pit	8	13	0	16	9	7
Other (see scrubber liquor, using cooling towers, recycle effluents, or combination)	8	12	18	11	13	13
Insufficient information	8	12	30	0	13	16
Number of plants contacted	29	8	49	22	33	141
Number of plants in industry (1976)	36	9	61	23	48	177

Source: Reference 10.

TABLE 6-8. SOURCES AND ESTIMATES OF PHOSPHORUS-CONTAINING AIR EMISSIONS FOR DIAMMONIUM PHOSPHATE PRODUCTION

Production activity	Controlled emission factor (g of particulate per 1 MT P_2O_5 in product)	% P_2O_5 in emissions	P emissions after controls (kg P/MT product)
Ammoniator-granulator	0.76	46	0.031
Dryer/cooler	0.75	46	0.030
Material transfer, product sizing and bagging:			
A. Controlled emission	0.03	46	0.001
B. Uncontrolled emission (fugitive dust losses)	2.2	46	0.087
Total			0.149

Source: Reference 14.

3. Calcination of phosphate rock without fusion.

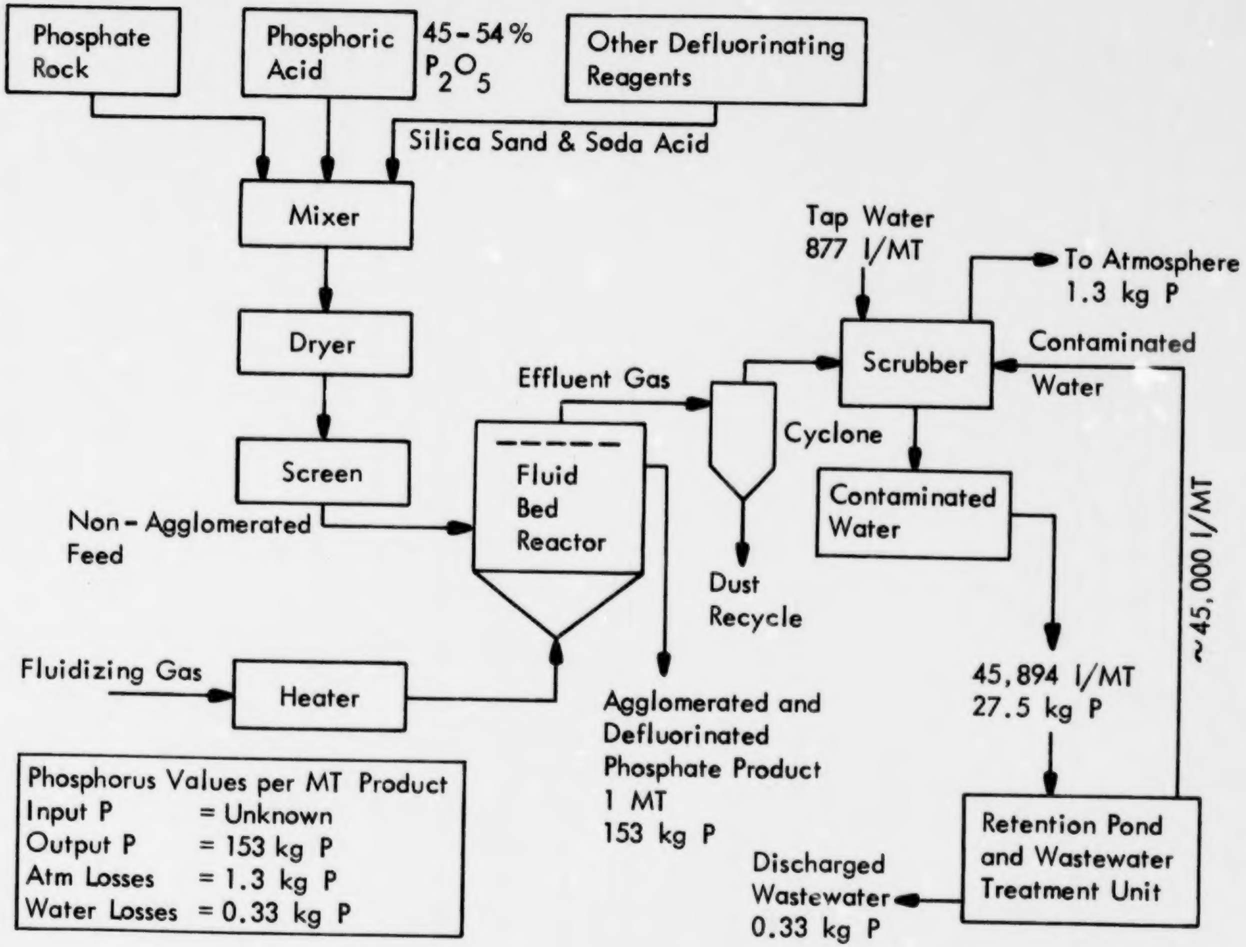
The third method, which has become the prominent domestic defluorination process, is discussed in this subsection. A representative flow diagram for this process is presented in Figure 6-9. The process basically involves the reaction of phosphate rock with phosphoric acid and defluorinating agents, followed by agglomeration and defluorination of the reaction mixture. The equation representative of the chemical reaction and fluorine release in the process is:[18]

$$Ca_{10}F_2(PO_4)_6 + H_2O + SiO_2 \longrightarrow 3Ca_3(PO_4)_2 + CaSiO_2 + 2HF\uparrow$$

The reader is referred to Reference 15 for a detailed discussion of this process.

Material balance data--This type of information was not found in the technical literature or obtained by contacts with industry representatives.

Assuming the products contain 76.5% tricalcium phosphate (35% P_2O_5), each metric ton of defluorinated phosphate rock contains 153 kg of phosphorus.


Phosphate Rock
Phosphoric Acid
45-54% P_2O_5
Other Defluorinating Reagents
Silica Sand & Soda Acid
Mixer
Dryer
Screen
Non-Agglomerated Feed
Fluid Bed Reactor
Effluent Gas
Cyclone
Dust Recycle
Fluidizing Gas
Heater
Agglomerated and Defluorinated Phosphate Product
1 MT
153 kg P
Tap Water
877 l/MT
Scrubber
To Atmosphere
1.3 kg P
Contaminated Water
Contaminated Water
45,894 l/MT
27.5 kg P
~45,000 l/MT
Retention Pond and Wastewater Treatment Unit
Discharged Wastewater
0.33 kg P
Phosphorus Values per MT Product
Input P = Unknown
Output P = 153 kg P
Atm Losses = 1.3 kg P
Water Losses = 0.33 kg P

Source: Reference 18.

Figure 6-9. Flow diagram for production of defluorinated phosphate rock.

A phosphorus mass balance showing values which apply for 1 MT of defluorinated phosphate rock product is as follows:

Input P 155.53 kg (estimated)

Outputs

Product	153 kg P		
Total wastewater losses	0.33 kg P		Total losses, 2.53 kg P
Atmospheric losses from scrubber	1.3 kg P	Total atm. losses, 2.2 kg P	
Atmospheric losses from material handling	0.9 kg P		

Wastewater effluent-- Since the process involves many trade secrets, only a minimal amount of information is reported on wastewater characterization in the published literature.[18] The types of wastewater involved are contaminated process water from stack-gas scrubbing and cleanup water from spills and leaks.[18]

The largest individual wastewater source is from water used in scrubbing contaminants from the effluent gas streams.[18] Most plants operate on a complete water recycle basis using a retention pond with make-up water added as required. Wastewater accumulations require treatment and discharge only during periods of excessive rainfall.

Because lime is added to the recirculating wastewater to control the pH, calcium phosphate, calcium sulfate, and calcium fluoride precipitate as a solid waste. The typical total usage of process water is reported to be about 45,900 liters/MT product.[18]

There are various sources of contaminated nonprocess wastewater. These sources involve accidental spills, accidental leaks due to process equipment failure and discharges from safety showers and personal safety equipment. Many manufacturers have demonstrated that spurious contaminations from leaks and spills and other sources can be held to a very low level.[18]

The EPA effluent limitations guidelines (BPCTCA) for processes which defluorinate phosphate rock recommend that the maximum average daily discharge concentration (for 30 consecutive days) of total phosphorus should not exceed 35 mg phosphorus per liter of wastewater.[18] It was assumed that this value would be the actual discharge concentration, that the plants would discharge wastewater for only 2.5 months each calendar year, and that the discharge rate would be the process water rate, or 45,900 liters/MT product. Thus, the estimated annual phosphorus discharge is 0.33 kg phosphorus per metric ton product.

Atmospheric emissions--Air emissions of phosphate rock occur in handling of the raw material. Also, emissions of defluorinated phosphate rock occur in the atmospheric vent from the scrubber used to treat off-gases from the reactor. These emissions were estimated on the basis of literature data[5/] and are discussed as follows.

Material handling--The total material handling is reported to have an uncontrolled particulate emission factor of 2 kg P_2O_5 per metric ton of product and it is assumed there is no emission control.[5/] Then, the estimated emission is approximately 0.9 kg phosphorus per metric ton of defluorinated phosphate rock.

Drying-agglomeration--From data on drying/cooling of calcium phosphate,[5/] it was assumed that the uncontrolled particulate emission is 30 kg P_2O_5 per metric ton of product and that the level of emission control is 90%. The estimated emission is 1.3 kg phosphorus per metric ton product. The total estimated air emissions from both sources is 2.2 kg phosphorus per metric ton of defluorinated phosphate rock.

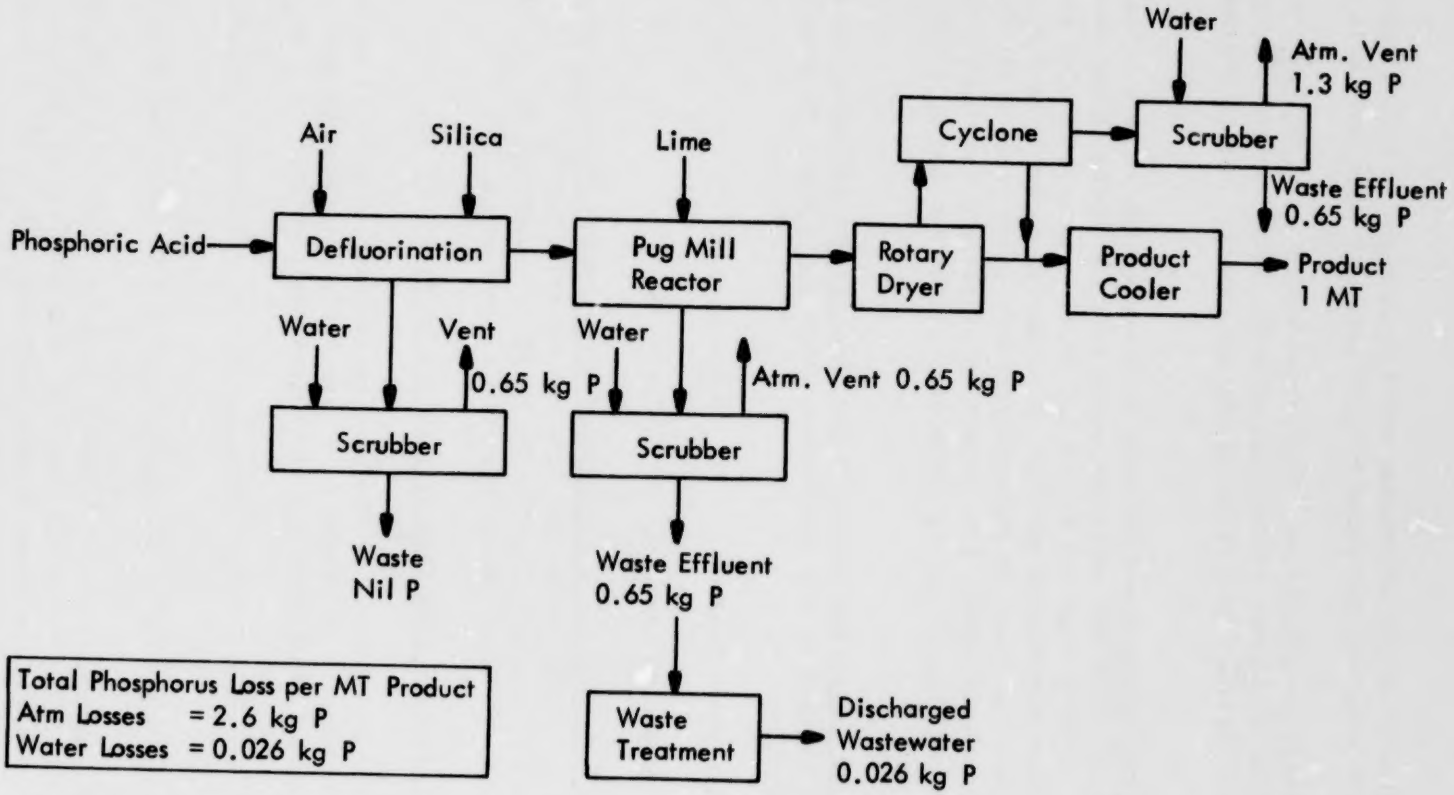
National emission for defluorinated phosphate rock production--Domestic production of this material in 1978 was about 272,000 MT. As shown later in Table 6-17, the calculated wastewater emission factor is 0.33 kg/MT and the air emission factor is 2.2 kg phosphorus per metric ton. The annual phosphorus discharge in plant effluent is calculated to be approximately 90 MT phosphorus. And the total air emission is estimated to be 600 MT phosphorus.

Production of Animal-Feed Calcium Phosphate (SIC No. 2819)--

Calcium phosphates are produced for use as a livestock feed-supplement by the neutralization of defluorinated phosphoric acid with lime. The product is usually a mixture of monocalcium phosphate, dicalcium phosphate (the principal component), and tricalcium phosphate. A representative process diagram is shown in Figure 6-10. For a detailed description of the process, the reader is referred to Reference 19.

Wastewater effluent--The acid defluorination step consists of treating heated phosphoric acid with finely-divided silica followed by aeration to liberate silicon tetrafluoride gas. Wet-scrubbers hydrolyze and collect this gas as fluosilicic acid and silicic acid. The raw wastewater generated in this treatment step does not contain a significant amount of phosphorus.[19/]

In the wet-scrubber used to treat off-gases from the pug mill reactor, the estimated raw waste load in the effluent is 4 kg of dissolved PO_4 per metric ton of product.[16/] The estimated total phosphorus load in raw wastewater is 0.65 kg phosphorus per metric ton product animal-feed.


Phosphoric Acid
Air
Silica
Defluorination
Water
Vent
0.65 kg P
Scrubber
Waste
Nil P
Lime
Pug Mill
Reactor
Water
Atm. Vent 0.65 kg P
Scrubber
Waste Effluent
0.65 kg P
Waste
Treatment
Discharged
Wastewater
0.026 kg P
Rotary
Dryer
Cyclone
Water
Scrubber
Atm. Vent
1.3 kg P
Waste Effluent
0.65 kg P
Product
Cooler
Product
1 MT
Total Phosphorus Loss per MT Product
Atm Losses = 2.6 kg P
Water Losses = 0.026 kg P

Source: Reference 19.

Figure 6-10. Flow diagram for production of animal-feed calcium phosphate.

The estimated amount of process water discharged is 6,720 liters/MT product for the combined operation of acid defluorination and solid scrubbing.

On the basis of EPA effluent limitation guidelines (BPCTCA), it is assumed that the maximum discharge of total phosphorus in wastewater is 0.026 kg/MT product animal-feed.[20] This value is the same as that for food-grade calcium phosphates.

Atmospheric emissions--These emissions are estimated on the basis of data from the literature.[5] Air emissions occur from the vents on the reactor-scrubber and from the scrubber used for drying and cooling operations. For each scrubber, the uncontrolled particulate emission is estimated to be 30 kg P_2O_5 per metric ton product, and the level of emission control is 90%. From these figures, 1.3 kg phosphorus per metric ton product is discharged from each scrubber; thus, the total air emission is 2.6 kg phosphorus per metric ton of product animal-feed.

Summary of phosphorus losses to environment--The following data are for phosphorus discharges to the environment which apply for 1 MT of animal-feed calcium phosphate.

Total wastewater losses	0.026 kg P
Total atmospheric losses	2.6 kg P

National emission for production of animal-feed-grade calcium phosphates--Based on the estimated production rate and emission factors for 1978, the phosphorus discharges are calculated to be 17 MT of phosphorus due to wastewater discharge and 1,651 MT of phosphorus from air emissions.

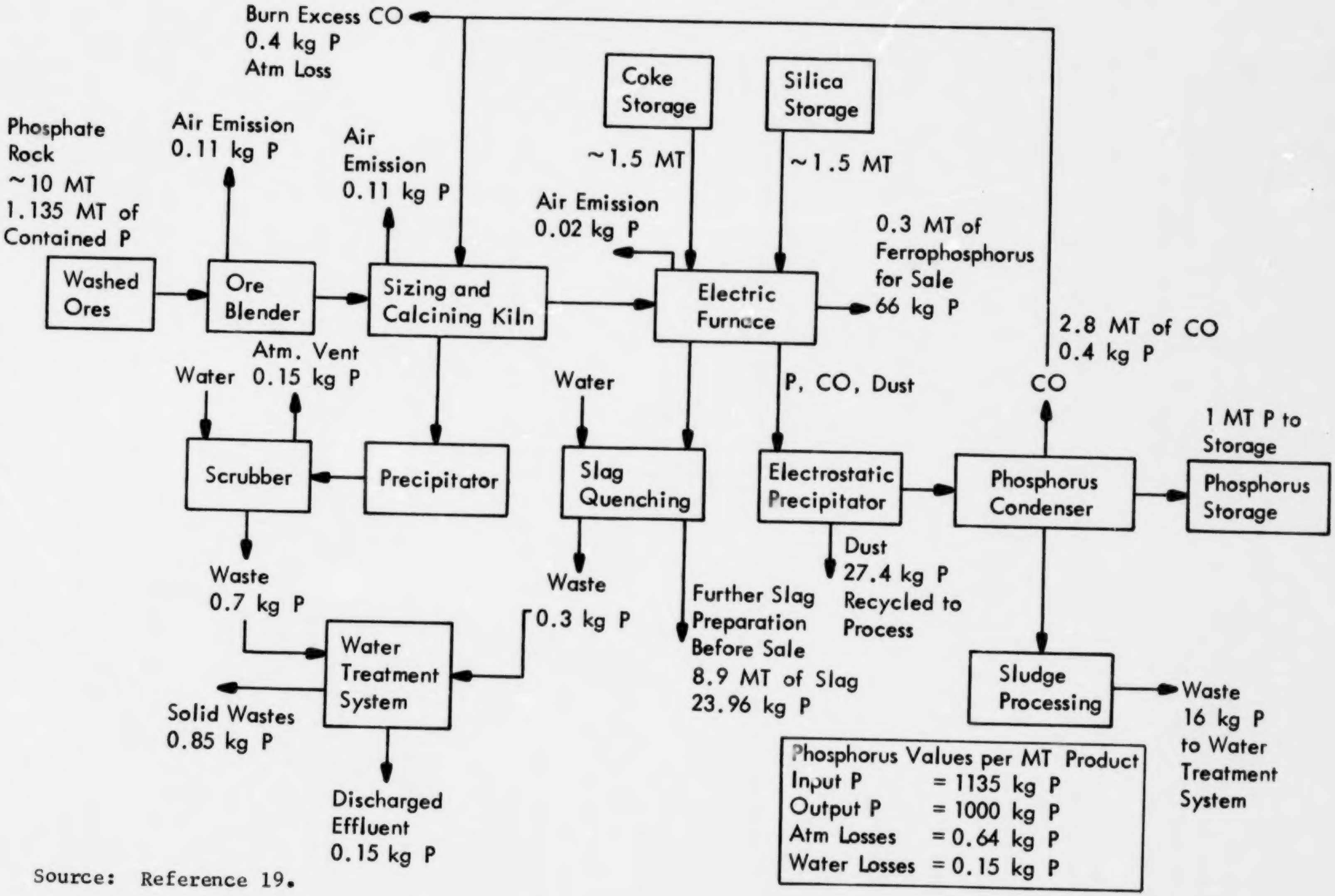
Production of Elemental Phosphorus (SIC No. 2819)--

Phosphorus is produced by the electric-furnace method, as shown in the representative process flowsheet in Figure 6-11. The raw materials are phosphate rock, silica, and coke. The simplified reaction is:

$$2Ca_3(PO_4)_2 + 6\ SiO_2 + 10\ C \longrightarrow P_4 + 6\ CaSiO_3 + 10\ CO$$

The production technology is described in detail in the literature.[11,19]

Material balance data--The quantity of total phosphate rock used depends on the analysis of the material. For 1 MT of phosphorus product, a typical grade of phosphate rock used as feed contains 2,600 kg of P_2O_5.[8] This value is equivalent to 1,135 kg phosphorus. Assuming a P_2O_5 concentration of 26%, the quantity of phosphate rock required is about 10,000 MT.[19]


Burn Excess CO
0.4 kg P
Atm Loss
Phosphate
Rock
~10 MT
1.135 MT of
Contained P
Washed
Ores
Air Emission
0.11 kg P
Ore
Blender
Air
Emission
0.11 kg P
Sizing and
Calcining Kiln
Coke
Storage
~1.5 MT
Silica
Storage
~1.5 MT
Air Emission
0.02 kg P
Electric
Furnace
0.3 MT of
Ferrophosphorus
for Sale
66 kg P
2.8 MT of CO
0.4 kg P
CO
Water
Atm. Vent
0.15 kg P
Scrubber
Precipitator
Water
Slag
Quenching
P, CO, Dust
Electrostatic
Precipitator
Phosphorus
Condenser
1 MT P to
Storage
Phosphorus
Storage
Waste
0.7 kg P
Waste
0.3 kg P
Further Slag
Preparation
Before Sale
8.9 MT of Slag
23.96 kg P
Dust
27.4 kg P
Recycled to
Process
Water
Treatment
System
Solid Wastes
0.85 kg P
Discharged
Effluent
0.15 kg P
Sludge
Processing
Waste
16 kg P
to Water
Treatment
System
Phosphorus Values per MT Product
Input P = 1135 kg P
Output P = 1000 kg P
Atm Losses = 0.64 kg P
Water Losses = 0.15 kg P

Source: Reference 19.

Figure 6-11. Flow diagram for production of elemental phosphorus.

For 1 MT of phosphorus product, a typical material balance shows the quantity of by-products to be: ferrophosphorus (Fe_2P), 0.3 MT; slag, 8.9 MT; and carbon monoxide, 2.8 MT. On the basis of reported data,[19] it was assumed that the ferrophosphorus contained 22% phosphorus, the slag contained 0.27% phosphorus, and the precipitator dust contained 21.9% phosphorus.

A phosphorus material balance was developed for the process flow diagram presented in Figure 6-11 and as follows (basis 1 MT phosphorus product):

Inputs	Kilograms of total phosphorus		
Phosphate rock	1,135		
Outputs			
Product	1,000		
Phossy water	16	Total water effluent, 17 kg P; discharged effluent, 0.15 kg P	Total P losses to environment, 0.79 kg
Slag quenching water	0.3		
Calcinor scrubber liquid	0.7		
Handling losses to atmosphere	0.11	Total atmospheric losses, 0.64 kg P	
Nodulizing losses to atmosphere	0.11		
Furnace losses to atmosphere	0.02		
Flare losses to atmosphere	0.4		
Recycled electrostatic precipitator dust	27.4		
Ferrophosphorus	66	Total in by-products, 89.98 kg P	
Slag (estimated by difference	23.96		
Total output	1,135		

Effluent wastewater--The phosphorus production industry is characterized by large amounts of raw process wastes, including scrubber and slag quenching wastewaters which contain substantial quantities of fluids, dissolved solids, and suspended solids.[19] Some plants have demonstrated control practices giving 97% or greater reduction in the raw waste load before discharge to the environment.[19]

In this study it was assumed that all phosphorus production plants treat the wastewater so as to meet the discharge standards of the best practicable control technology currently available. The discharge standard specifies that the average of daily values for 30 consecutive days shall not exceed 0.15 kg total phosphorus per metric ton product.[20/] It was assumed that the plants operate with this maximum allowable discharge of phosphorus in effluent.

Air emission[5/]--The phosphate rock feed must be processed through a calcining kiln operation before the rock can be used as a furnace charge. Air emissions of rock dust are involved in the handling and calcining operations. The calcining step is a significant generator of P_2O_5 emissions and scrubbers are often employed to reduce particulate emissions.

There are some general sources of P_2O_5 emissions in the operation of the electric furnace. Fumes of P_2O_5 tend to leak out of the furnace around the electrodes and the feed bins. Another emission source is the furnace tapping operation. Since visible quantities of P_2O_5 fumes can result during tapping of slag and ferrophosphorus, many operations have installed hood and ventilation systems designed to capture the fumes and direct them through gas scrubbers.

Other P_2O_5 emissions are from the handling of collected dusts from air pollution control devices and from the storage and transfer of phosphorus. Since these operations are infrequent and the quantities handled are small, the total emissions from the sources are estimated to be negligible.

The burning of excess carbon monoxide in a flare results in air pollution by phosphorus pentoxide (P_2O_5).

Estimates of the phosphorus emissions to the atmosphere were performed according to the procedures described previously on page 98. Results of these estimates are summarized in Table 6-9. The estimated total phosphorus discharge to the atmosphere is 0.64 kg/MT product.

National emission for elemental phosphorus production--The estimated production rate for elemental phosphorus in 1978 is 462,000 MT (see Table 6-17).

The approximate discharge of phosphorus in wastewater is estimated to be 69 MT phosphorus and the air emissions are estimated to be approximately 296 MT phosphorus.

Production of Phosphoric Acid by the Dry Process (SIC No. 2819)--

A typical flowsheet is presented in Figure 6-12. Elemental phosphorus is converted to orthophosphoric acid (H_3PO_4) by the following overall reaction.

$$P_4 + 5O_2 + 6H_2O \longrightarrow 4H_3PO_4$$

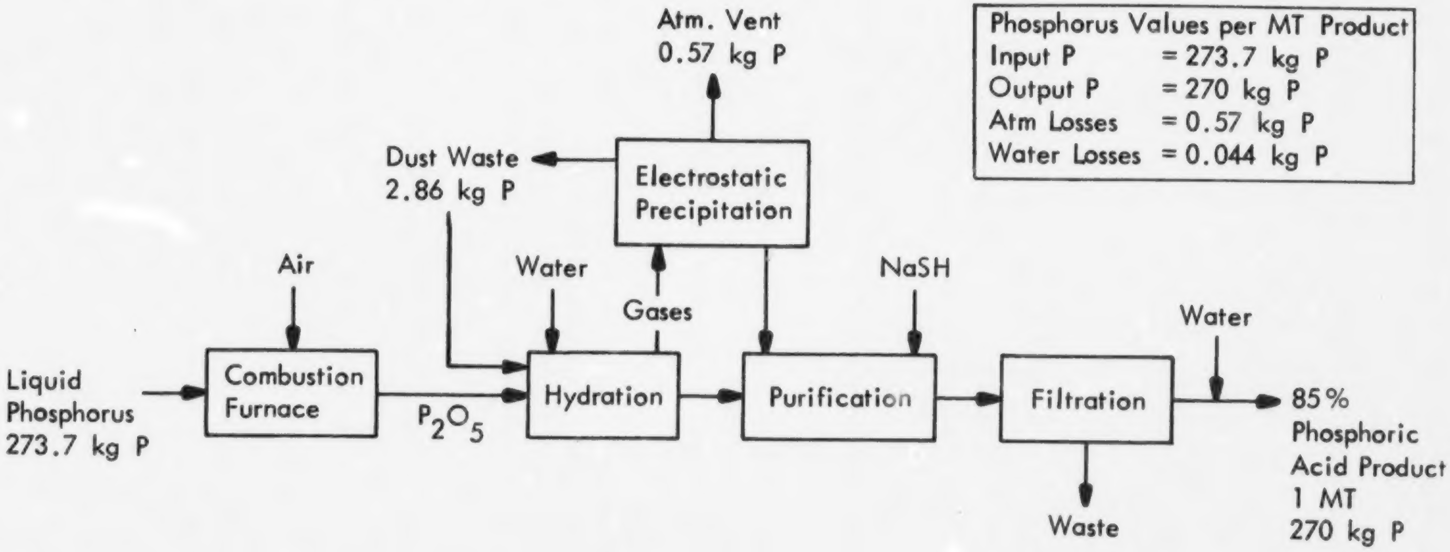
Phosphorus is often converted to phosphoric acid at locations other than the original point of production. Detailed descriptions of this process are presented in the literature.[5,11,19/]

TABLE 6-9. SOURCES AND ESTIMATES OF PHOSPHORUS-CONTAINING AIR EMISSIONS FOR PRODUCTION OF ELEMENTAL PHOSPHORUS

Production activity	Uncontrolled particulate emission factor (kg/MT)	% P_2O_5 in emissions	Estimated level of emission control (%)	P emissions after controls (kg P/MT product)
Phosphate rock handling	1	25	0	0.11
Calcining kiln (nodulizing)	0.65	a/	60	0.11
Furnace operations	0.5	a/	90	0.02
Flares	0.9	a/	0	0.40
Total				0.64

a/ Emission factor includes % P_2O_5.

Source: Reference 3.


Phosphorus Values per MT Product
Input P = 273.7 kg P
Output P = 270 kg P
Atm Losses = 0.57 kg P
Water Losses = 0.044 kg P
Atm. Vent 0.57 kg P
Dust Waste 2.86 kg P
Electrostatic Precipitation
Air
Water
Gases
NaSH
Water
Liquid Phosphorus 273.7 kg P
Combustion Furnace
P_2O_5
Hydration
Purification
Filtration
85% Phosphoric Acid Product 1 MT 270 kg P
Waste

Note:

Estimated Total Phosphorus Release to Environment as Treated Wastewater from Cleanup of Leaks and Spills is 0.044 kg

Source: Reference 19.

Figure 6-12. Flow diagram for production of phosphoric acid (dry process).

Material balance data--In a typical process, the production of 1 MT of product acid containing 85% H_3PO_4 requires 273.7 kg of phosphorus as raw material.[12]

A phosphorus mass balance showing values which apply for 1 MT of phosphoric acid follows:

Input		
Phosphorus	273.7 kg P	
Outputs		
Product	270 kg P	
Total wastewater discharge	0.044 kg P	Total accounted for P losses, 0.614 kg
Total atmospheric losses	0.57 kg P	
Dust waste (recycled)	2.86 kg P	
Unaccounted for P	0.226 kg P	

Wastewater effluent--No aqueous waste streams are generated in this process.

In spite of good housekeeping practices, losses of phosphoric acid (H_3PO_4) by leaks and spills can amount to an average of 1 kg of H_3PO_4 per metric ton of product.[19] The estimated phosphorus is 0.27 kg phosphorus per metric ton product.

It was assumed that plant cleanup wastewater containing this phosphorus is treated in pollution control equipment and then discharged to the environment. On the basis of the EPA effluent limitation guidelines (BPCTCA), the estimated phosphorous loss to the environment in wastewater is 0.044 kg total phosphorus per metric ton product.[20]

Atmospheric emissions--Phosphoric acid mist is a pollutant in the tail gas vented from the hydration and electrostatic precipitation steps. Although all plants are equipped with some type of acid mist collection systems, some mist does escape to the atmosphere.

An estimate of the phosphorus emissions as H_3PO_4 mist to the atmosphere from this process was made on the basis of literature data.[5] For the hydration step, the estimated particulate emission factor after controls is 1.3 kg P_2O_5 per metric ton product or 0.57 kg phosphorus per metric ton product.

Solid waste--Most of the phosphorus in the off-gases from the hydration step is recovered in the electrostatic precipitator and is contained in the dust waste.

It is assumed that the phosphorus output not accounted for in the finished product, vented mist, and leaks and spills occurs in the dust from the electrostatic precipitator. On this basis the contained phosphorus in this dust is 2.86 kg phosphorus per metric ton product. It was assumed that this dust is recycled to the process.

National emissions for dry process phosphoric acid production--For 1978, the estimated total domestic production of dry process phosphoric acid is equivalent to 833,000 MT of contained P_2O_5. Assuming an acid concentration of 61.87% P_2O_5 (86% H_3PO_4) the estimated production of dry process phosphoric acid is 1,346,400 MT.

The estimated total emission from wastewater discharge are 60 MT phosphorus; about 770 MT of phosphorus are contained in the total annual air emissions.

Phosphorus Pentoxide Production (SIC No. 2819)--

The production of solid anhydrous phosphorus pentoxide involves burning liquid phosphorus in an excess of air:

$$P_4 + 5O_2 \longrightarrow 2P_2O_5$$

Figure 6-13 is a representative flow diagram for this process; details of the operation are reported in Reference 19.

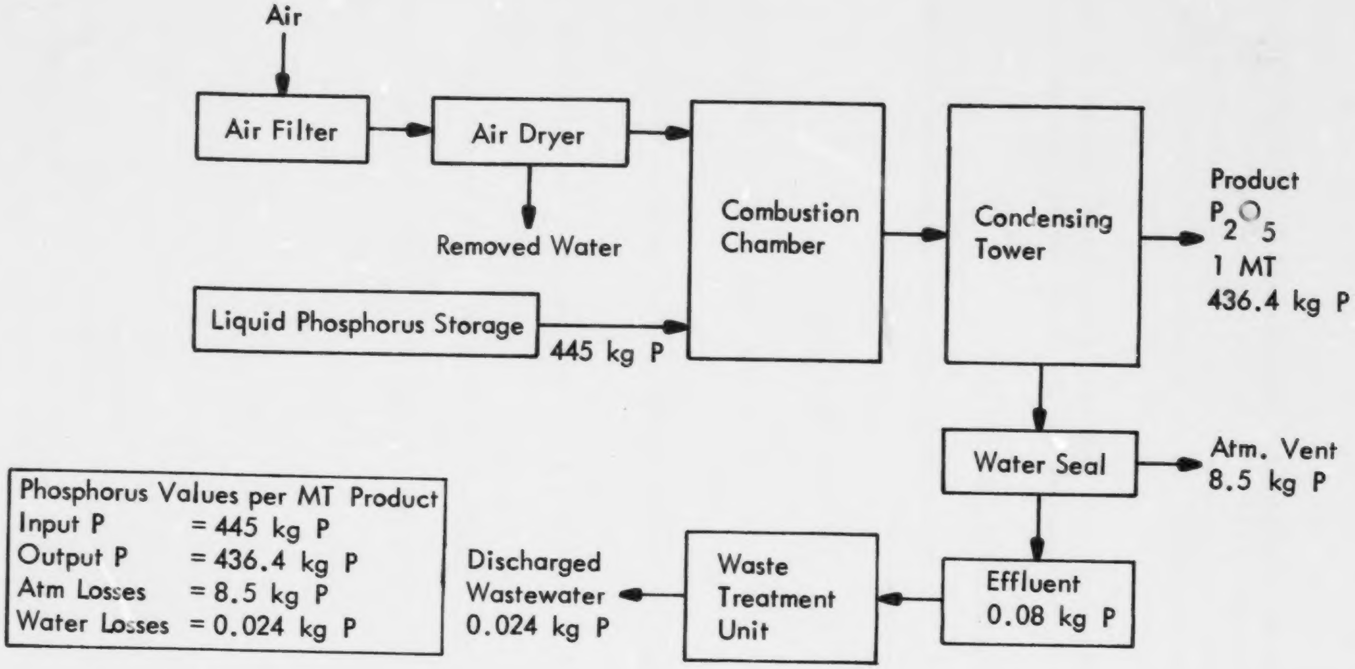
Material balance data--The process yield on raw material phosphorus was assumed to be 98%.[19]

The phosphorus contained in 1,000 kg of product P_2O_5 is calculated to be 436.4 kg.

The phosphorus raw material required is estimated to be 445 kg.

A phosphorus mass balance showing values which apply for 1 MT of phosphorus pentoxide product follows:

Input		
Phosphorus	445 kg P	
Outputs		
Product	436.4 kg P	
Total wastewater losses	0.024 kg P	Total accounted for P losses, 8.524 kg
Total atmospheric losses	8.5 kg P	
Unaccounted for P	0.076 kg P	


Air
Air Filter
Air Dryer
Removed Water
Liquid Phosphorus Storage
445 kg P
Combustion Chamber
Condensing Tower
Product
P_2O_5
1 MT
436.4 kg P
Water Seal
Atm. Vent
8.5 kg P
Effluent
0.08 kg P
Waste Treatment Unit
Discharged Wastewater
0.024 kg P
Phosphorus Values per MT Product
Input P = 445 kg P
Output P = 436.4 kg P
Atm Losses = 8.5 kg P
Water Losses = 0.024 kg P

Source: Reference 19.

Figure 6-13. Flow diagram for production of phosphorus pentoxide.

Wastewater effluent--The typical contaminated wastewater from the tail seals for the condensing tower is reported to contain 0.25 kg of H_3PO_4 (100%) per metric ton product.[19] On this basis, the quantity of phosphorus contained in this waste stream is estimated to be 0.08 kg phosphorus per metric ton of product.

It was assumed that this waste is treated in a pollution control unit and that the discharged wastewater conforms to the BPCTCA effluent limitation guidelines which specify 0.024 kg of contained phosphorus per metric ton product.[20]

Atmospheric emissions--The estimated phosphorus losses due to handling, spills, and leaks are calculated from a material balance to be 8.5 kg phosphorus per metric ton product.

National emission for phosphorus pentoxide production--Domestic production of this compound in 1978 amounted to about 8,000 MT and the estimated emission factors are 0.024 and 8.5 kg phosphorus per metric ton of product for wastewater discharge and air emissions, respectively. The estimated total annual phosphorus quantities in wastewater discharge are 0.2 MT and 68 MT in air emissions.

Phosphorus Trichloride Production (SIC No. 2819)--

Phosphorus trichloride (PCl_3) is manufactured directly from the elements according to the reaction.[19]

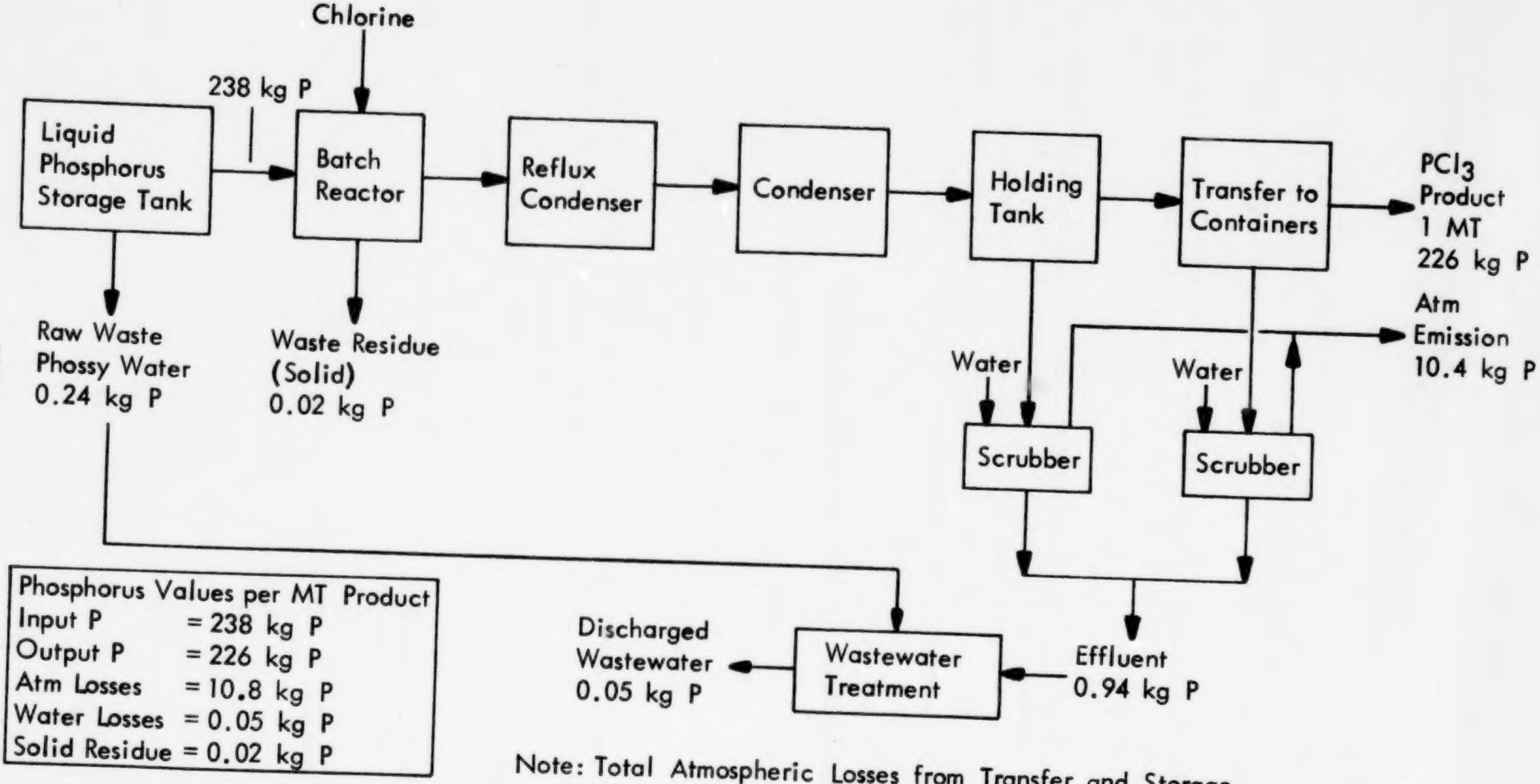
$$P_4 \text{ (liquid)} + 6Cl_2 \text{ (gas)} \longrightarrow 4PCl_3 \text{ (liquid)}$$

A representative flow diagram for this process is given in Figure 6-14. Details of process operations are described in References 12 and 19. Phosphorus trichloride is used as a raw material in the production of phosphorus oxychloride pesticide intermediates, phosphate esters, surfactants, and organic alkyl chlorides.

Material balance data--Published information shows that a typical material balance for the process is as follows:[12]

Raw materials	Kilogram	Product	Kilogram
Phosphorus	238	PCl	1,000
Chlorine	815		

The phosphorus content of the pure product is 22.55%. Then, the amount of phosphorus in 1,000 kg of PCl_3 is 225.5 kg.


Chlorine
238 kg P
Liquid Phosphorus Storage Tank
Batch Reactor
Reflux Condenser
Condenser
Holding Tank
Transfer to Containers
PCl_3 Product
1 MT
226 kg P
Atm Emission
10.4 kg P
Raw Waste Phossy Water
0.24 kg P
Waste Residue (Solid)
0.02 kg P
Water
Water
Scrubber
Scrubber
Discharged Wastewater
0.05 kg P
Wastewater Treatment
Effluent
0.94 kg P

Phosphorus Values per MT Product
Input P = 238 kg P
Output P = 226 kg P
Atm Losses = 10.8 kg P
Water Losses = 0.05 kg P
Solid Residue = 0.02 kg P

Note: Total Atmospheric Losses from Transfer and Storage of P and PCl_3 are 0.45 kg P/MT of Product PCl_3

Source: Reference 19.

Figure 6-14. Flow diagram for production of phosphorus trichloride.

A phosphorus mass balance showing values which apply for 1 MT of phosphorus trichloride product follows:

Input		
Phosphorus	238 kg P	
Outputs		
Product	226 kg P	
Total wastewater losses	0.05 kg P	Total accounted for P losses, 10.87 kg
Total atmospheric losses	10.8 kg P	
Total solid waste residue	0.02 kg P	
Unaccounted for P	1.13 kg P	

Wastewater effluent--Elemental phosphorus is transported and stored under a water blanket to prevent combustion on exposure to air. Therefore, phossy water is a raw waste material at plants using phosphorus. The standard raw phossy water wastes are caused by surges or anomolies in the storage tank water level control system rather than to the direct discharge of all displaced water. This water contains colloidal phosphorus as well as phosphoric acid.[19]

No direct process aqueous wastes are generated. Raw wastes arise from phosphorus storage and transfer, wet-scrubbing of gases, vessel cleaning, and leaks and spills.[19]

Some spill and leak losses (atmospheric) of PCl_3 occur during transfer operations. The tail gases vented to atmosphere from the scrubbers also contain some PCl_3.

The waterborne raw wastes contain H_3PO_3, H_3PO_4, and HCl, which are formed by hydrolysis of PCl_3 contained in the waste. The acid wastes (H_3PO_3, H_3PO_4) from washing tank cars and tank trucks are very small.

The waterborne raw waste from the scrubber for distillation tail gases is reported to contain 2.5 kg of H_3PO_3 per metric ton product.[19] The estimated phosphorus content is calculated to be 0.94 kg phosphorus per metric ton product.

For each metric ton of phosphorus consumed in the production process, 1 kg of phosphorus is discharged in the phossy water waste.[19] However, the production of 1 MT of phosphorus trichloride requires only 0.238 MT of phosphorus so that the total phosphorus discharged in the phossy water waste would be 0.238 kg/MT product. Combining this figure with 0.94 kg stated above gives a total phosphorus content in wastewater of 1.18 kg phosphorus per metric ton product.

It is assumed that the wastewater is treated in some fashion with pollution control equipment so that the phosphorus contained in treated discharged waste is 0.05 kg/MT of PCl_3 product. This value is specified in the EPA effluent limitation guidelines (BPCTCA).[20]

Atmospheric emissions--The transfer and storage of phosphorus and phosphorus trichloride account for the equivalent loss of 2 kg of PCl_3 per metric ton product.[19] Then, the corresponding emission of phosphorus is calculated to be 0.45 kg phosphorus per metric ton product.

The amount of phosphorus discharged from scrubber vents is calculated, by difference, from a process material balance to equal 10.36 kg/MT product. Thus, the estimated total atmospheric phosphorus discharge is 10.8 kg/MT of PCl_3.

Solid waste residue--Solid waste, which is removed periodically from the reactor-still, reportedly contains 0.1 kg of PCl_3 per metric ton product.[19] The amount of phosphorus contained in this waste would be 0.02 kg phosphorus per metric ton product. No information was obtained concerning the final disposal of this solid waste.

National emission for phosphorus trichloride production--Application of the 1978 production data and the emission factors listed in Table 6-17 results in the following estimated plant discharges of phosphorus:

Wastewater: 5 MT phosphorus

Air emission: 1,002 MT phosphorus

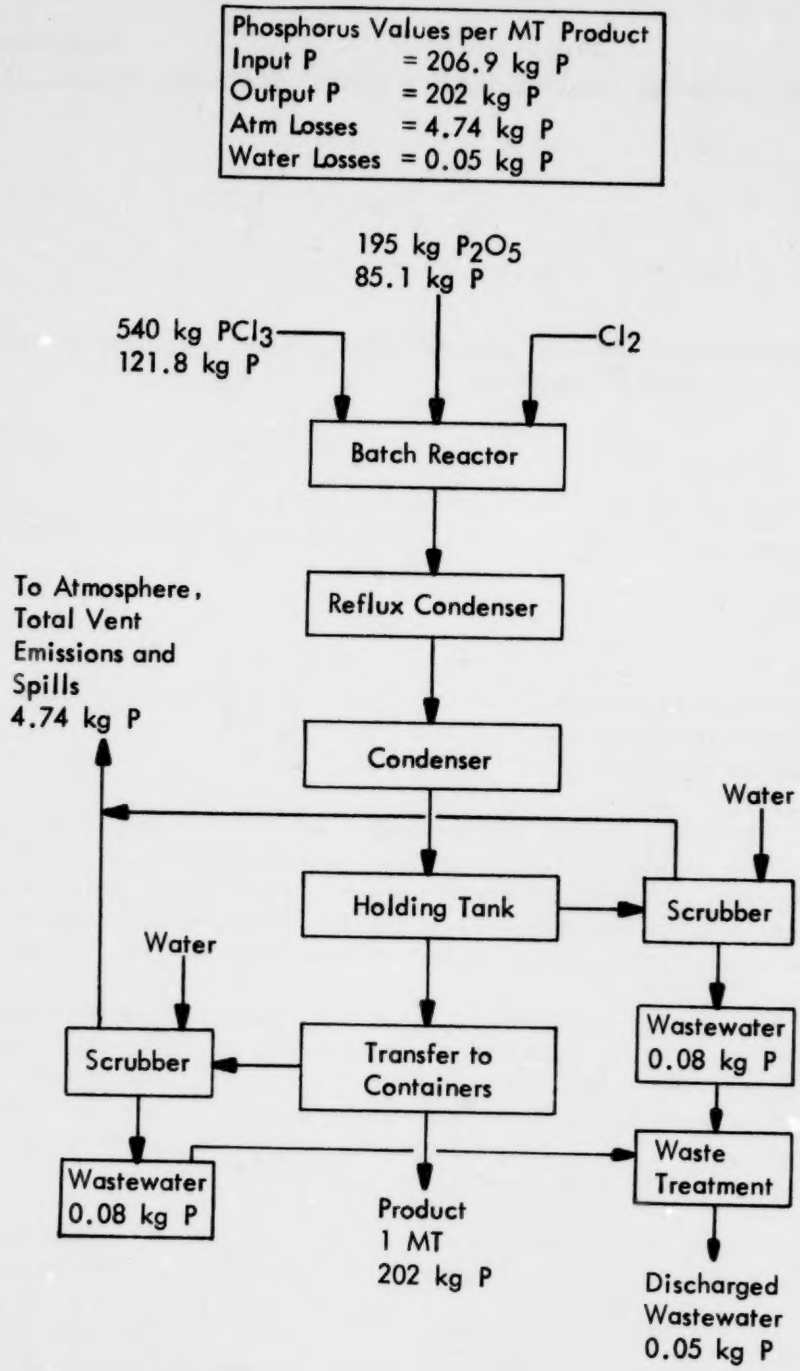
Phosphorus Oxychloride Production (SIC No. 2819)--

Phosphorus oxychloride, which is utilized in the preparation of pharmaceutical chemicals and organic phosphate esters, is produced commercially by the reaction of liquid phosphorus trichloride, chlorine gas, and solid phosphorus pentoxide.[19]

$$3PCl_3 + 3Cl_2 + P_2O_5 \longrightarrow 5POCl_3$$

A typical process flow diagram is given in Figure 6-15. Details of the process operations are discussed in References 12 and 19. Phosphorus oxychloride is used as a raw material in the production of tricresyl and triphenyl phosphates, cyclic esters, and acyclic esters.

Material balance data--Data taken from Reference 12 show the following representative material balance for this process:


Phosphorus Values per MT Product
Input P = 206.9 kg P
Output P = 202 kg P
Atm Losses = 4.74 kg P
Water Losses = 0.05 kg P
195 kg P_2O_5
85.1 kg P
540 kg PCl_3
121.8 kg P
Cl_2
Batch Reactor
Reflux Condenser
To Atmosphere, Total Vent Emissions and Spills
4.74 kg P
Condenser
Water
Holding Tank
Scrubber
Water
Wastewater
0.08 kg P
Scrubber
Transfer to Containers
Waste Treatment
Wastewater
0.08 kg P
Product
1 MT
202 kg P
Discharged Wastewater
0.05 kg P

Source: Reference 19.

Figure 6-15. Flow diagram for production of phosphorus oxychloride.

Raw materials	Kilogram	Phosphorus content (kg)	Product	Kilogram	Phosphorus content (kg)
PCl_3	540	121.8	$POCl_3$	1,000	202
Cl_2	280	-			
P_2O_5	195	85.1			

A phosphorus mass balance showing values which apply for 1 MT of phosphorus oxychloride product follows:

Inputs

Phosphorus pentoxide	85.1 kg P	Total P input, 206.9 kg
Phosphorus trichloride	121.8 kg P	

Outputs

Product	202 kg P	Total P losses, 4.79 kg
Total wastewater losses	0.05 kg P	
Total atmospheric losses	4.74 kg P	
Unaccounted for P	0.11 kg P	

Phosphorus losses in the process occur in the effluent from the wet-scrubber for the reactor-still and in the effluent from the scrubber for off-gases from product transfer to containers.[19] Also, small amounts of phosphorus release occur in container cleaning operations. In the presence of the water in these effluent wastes, $POCl_3$ is hydrolyzed to form H_3PO_4 and HCl.

Some plants filter the product; when this practice is followed, the used filter elements are first washed to hydrolyze the residual $POCl_3$ and the disposable elements landfilled. The amount of solids retained on the filter elements is a very small fraction of the weight of the filter element. These elements are washed in a small drum so that only a small quantity of acid wastes is involved compared to the scrubber waste load.[19]

A small amount of residue (mostly glassy phosphates) accumulates in the reactor.[19] Twice each year this residue is washed out of the reactor with hot water.[19]

Wastewater effluent--The water scrubber for product transfer to containers reportedly collects about 0.15 kg of H_3PO_4 per metric ton product.[19] It is assumed that the wastes from returnable container cleaning operations (0.1 kg H_3PO_4) are discharged along with the scrubber wastewater for a total of 0.2 kg H_3PO_4 or a phosphorus discharge in the effluent of 0.08 kg phosphorus per metric ton product.

The water scrubber for the distillation operation typically collects 0.25 kg of H_3PO_4 (100%) per metric ton of product.[19] Then, the phosphorus contained in this acid is 0.08 kg phosphorus per metric ton of product.

Thus, the estimated total phosphorus in wastewater effluent is 0.16 kg phosphorus per metric ton product. This waste is processed in a waste treating unit and the discharged phosphorus in wastewater is 0.05 kg/MT which meets the EPA effluent guidelines (BPCTCA).[20]

Atmospheric emissions--The total atmospheric loss of phosphorus from scrubber vents and spills is estimated, by difference, from the material balance to be 4.74 kg phosphorus per metric ton of product.

Solid wastes--The total solid wastes (glassy phosphates) are reported to be less than 0.05 kg/MT product. The phosphorus content of these wastes is unknown.[19]

National emission for phosphorus oxychloride production--The estimated phosphorus losses to environment based on production and emission data in Table 6-17 are:

Wastewater: 4 MT phosphorus and

Air emission: 376 MT phosphorus

Phosphorus Pentasulfide Production (SIC No. 2819)--

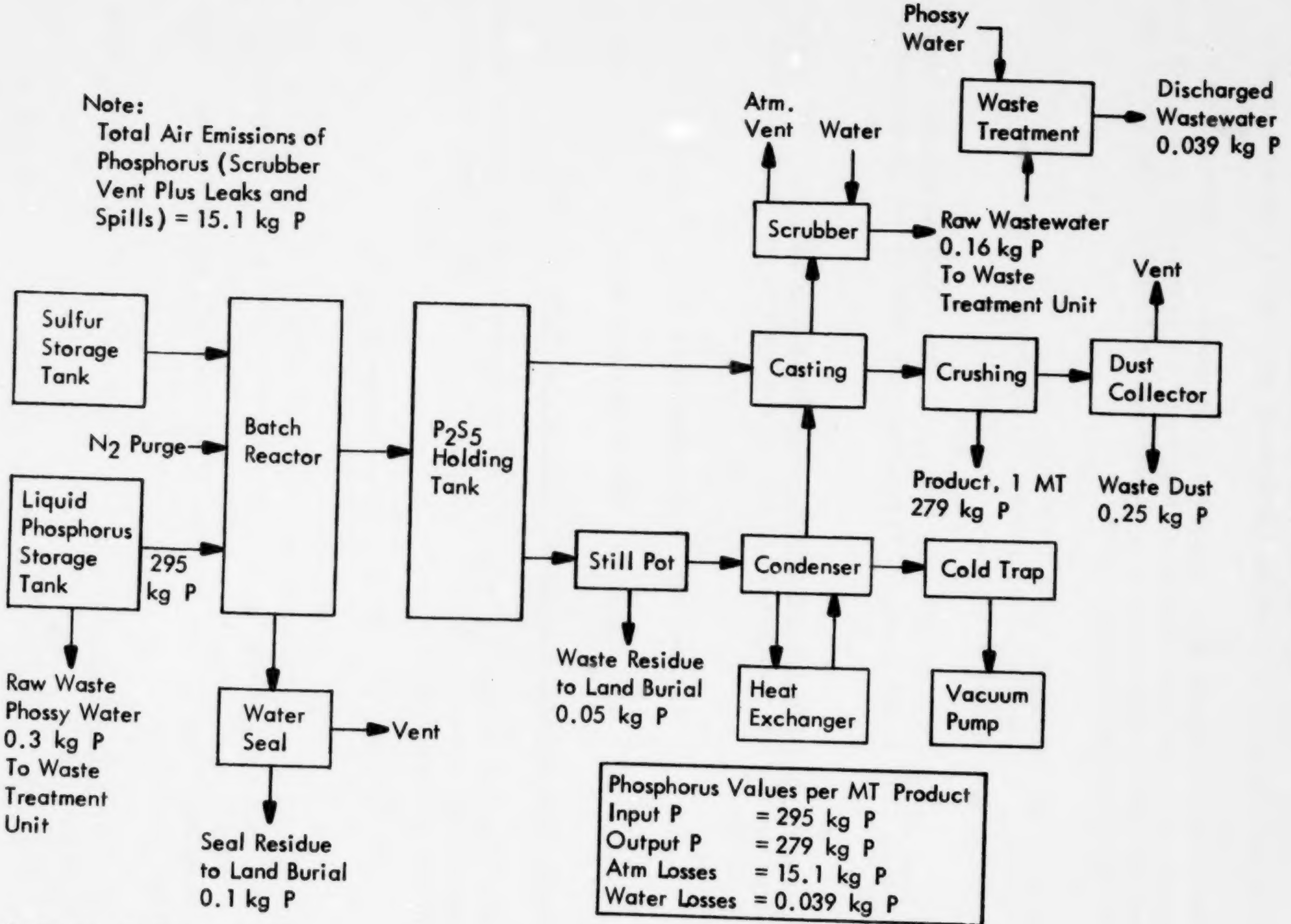
The standard commercial process for production of phosphorus pentasulfide, as shown in the flow diagram in Figure 6-16, is by the direct reaction of the elements in liquid form:

$$P_4 + 10\ S \longrightarrow 2P_2S_5$$

The product is used principally for the manufacture of lubricating oil additives and as a raw material in the organophosphorus pesticide industry. A discussion of processing details is given in the technical literature.[19] Phosphorus pentasulfide is used in the production of lube oil additives, pesticides, and flotation agents.

Material balance data--Input and output data for this process were obtained from Reference 12.

Raw materials	Kilogram	Product	Kilogram	Phosphorus content (kg)
Phosphorus	295	P_2S_5	1,000	278.7
Sulfur	760			


Phossy Water
Waste Treatment
Discharged Wastewater 0.039 kg P
Note: Total Air Emissions of Phosphorus (Scrubber Vent Plus Leaks and Spills) = 15.1 kg P
Atm. Vent
Water
Scrubber
Raw Wastewater 0.16 kg P To Waste Treatment Unit
Vent
Sulfur Storage Tank
Batch Reactor
P_2S_5 Holding Tank
Casting
Crushing
Dust Collector
N_2 Purge
Product, 1 MT 279 kg P
Waste Dust 0.25 kg P
Liquid Phosphorus Storage Tank
295 kg P
Still Pot
Condenser
Cold Trap
Raw Waste Phossy Water 0.3 kg P To Waste Treatment Unit
Water Seal
Vent
Waste Residue to Land Burial 0.05 kg P
Heat Exchanger
Vacuum Pump
Seal Residue to Land Burial 0.1 kg P
Phosphorus Values per MT Product
Input P = 295 kg P
Output P = 279 kg P
Atm Losses = 15.1 kg P
Water Losses = 0.039 kg P

Source: Reference 19.

Figure 6-16. Flow diagram for production of phosphorus pentasulfide.

A phosphorus mass balance showing values which apply for 1 MT of phosphorus pentasulfide product follows.

Input		
Phosphorus	295 kg P	
Outputs		
Product	279 kg P	
Total wastewater losses	0.039 kg P	Total P losses, 15.539 kg
Total atmospheric losses	15.1 kg P	
Total solid wastes to landfill	0.4 kg P	
Unaccounted for P	0.461 kg P	

Wastewater effluent--In the casting of liquid P_2S_5 to form the solid product, fumes from the burning liquid (auto-ignited) are treated in a wet-scrubber. The waste water discharged from this scrubber contains phosphorus in the form of H_3PO_3 and H_3PO_4 (0.5 kg of H_3PO_3 and H_3PO_4/MT of product). The amount of phosphorus in this waste can be estimated, assuming all acid to be H_3PO_4, at 0.16 kg phosphorus per metric ton product.[19]

Some phosphorus losses occur in the discharge of phossy water during the material handling operations for liquid phosphorus. The phosphorus in this wastewater is in the form of colloidal phosphorus as well as H_3PO_3 and H_3PO_4. The quantity of total phosphorus in discharged phossy water is 1 kg phosphorus per metric ton of phosphorus consumed in the process.[19] On this basis, the total discharged phosphorus in phossy water is approximately 0.3 kg phosphorus per metric ton product. The estimated total phosphorus content in wastewater is 0.46 kg phosphorus per metric ton product.

It was assumed that the combined wastewater streams are treated in a pollution control unit and that the discharged wastewater conforms to the EPA effluent guidelines (BPCTCA) so that 0.039 kg total phosphorus is lost per metric ton product.[19]

Atmospheric emissions--Losses of phosphorus occur as P_2O_5 fumes emitted to the air from the vent on the wet-scrubber unit.[19] Other air emissions include spills and leaks of phosphorus and of finished product.

Solid wastes--Water seals on the batch reactor vent lines accumulate a mixture of lower phosphorus sulfides and phosphorus mud. This residue, which is hazardous and flammable, is typically disposed of by land-burial. These wastes contain about 0.15 kg of unidentified solid compounds per metric ton of product.[19] Assuming these wastes to be 50% phosphorus mud, and 50% phosphorus sulfide, the total phosphorus content can be estimated at approximately 0.1 kg phosphorus per metric ton product.

The dust collected by a dry cyclone separator from the off-gas stream for the P_2S_5 crushing operation is a solid waste material; the quantity of this dust amounts to about 1 kg/MT product.[19] Assuming that the dust contains 90% P_2S_5, the estimated phosphorus content is calculated to be 0.25 kg phosphorus per metric ton of product.

The still pot for the vacuum distillation step accumulates impurities including carbon, iron phosphate, sulfur compounds, arsenic pentasulfide, and glassy phosphates.[19] The entire still pot residue amounts to about 0.5 kg/MT product. This pot residue is removed periodically and the solids broken up and buried.[19] Assuming that the glassy phosphates comprise one-half of the total waste and that the phosphates consist of $FePO_4$, the estimated content of phosphorus is 0.05 kg phosphorus per metric ton product.

The estimated total phosphorus contained in solid wastes is 0.4 kg phosphorus per metric ton product.

National emission for phosphorus pentasulfide production--On the basis of production rate and emission data, the estimated phosphorus discharges are:

Wastewater: 3 MT,

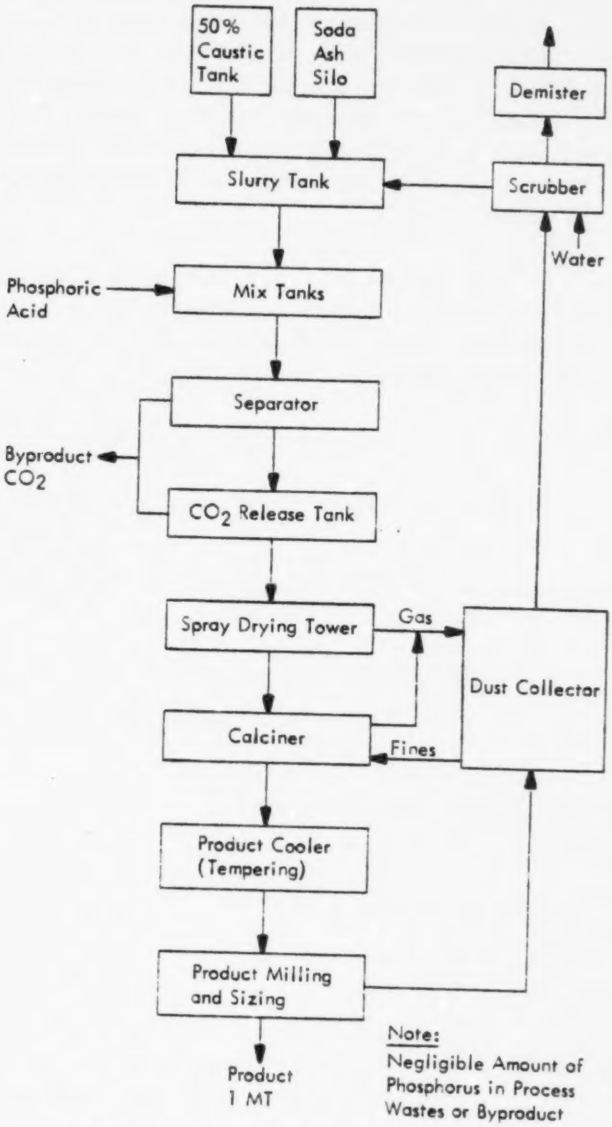
Air emissions: 1,160 MT, and

Solid wastes: 31 MT phosphorus.

Sodium Tripolyphosphate (STPP) Production (SIC No. 2841)--

This product is manufactured by the neutralization of phosphoric acid (normally furnace acid) by soda ash or by caustic soda and soda ash, with subsequent calcination of the dried mono- and di-sodium phosphate crystals.[19] The standard manufacturing process is presented in Figure 6-17. Principal uses for this product are in detergents and in water supplies as a means of controlling corrosion. The product is also used in some softened waters for stabilization of calcium carbonate to eliminate the need for recarbonization.[31]

Several plants of this type are reported to have no process wastes.[19] Collected dust from the spray dryer effluent stream is combined with the spray dryer solid product stream. Water utilized for subsequent scrubbing of the gas stream from the spray dryer is recycled to the mix area and used as process water in the neutralization step. Cooling air used for tempering the product is vented into the spray dryer vent line upstream of the scrubbing operation. These pollution control techniques are generally applicable throughout the industry. The effluent guideline standard (BPCTCA) is no discharge of wastewater.[19] Thus, it is concluded that no significant phosphorus releases to the environment occur from this process.


50% Caustic Tank
Soda Ash Silo
Demister
Slurry Tank
Scrubber
Water
Phosphoric Acid
Mix Tanks
Separator
Byproduct CO_2
CO_2 Release Tank
Spray Drying Tower
Gas
Dust Collector
Calciner
Fines
Product Cooler (Tempering)
Product Milling and Sizing
Product 1 MT
Note:
Negligible Amount of Phosphorus in Process Wastes or Byproduct

Source: Reference 19.

Figure 6-17. Flow diagram for production of sodium tripolyphosphate.

Production of Sodium Phosphates - SIC No. 2841 (Excluding STPP)--

These products are used principally for detergent manufacturing and water treatment. Detergent industries generally require high purity sodium phosphates; this purity standard has greatly limited the use of wet-process acid, which has several impurities, as a phosphate source for this industry. Normally, phosphoric acid manufactured by the furnace process is used because of its higher purity. However, one company does purify wet-process acid to the extent necessary to allow its use in the manufacture of sodium phosphate compounds for detergent manufacture.[18]

As an example for this industry, this subsection will examine the production of sodium phosphates from furnace phosphoric acid and sodium carbonate. The process flow diagram is shown in Figure 6-18. The reader is referred to Reference 12 for a detailed process description. The basic reactions are:

$$Na_2CO_3 + H_3PO_4 \longrightarrow Na_2HPO_4 + CO_2\uparrow + H_2O$$

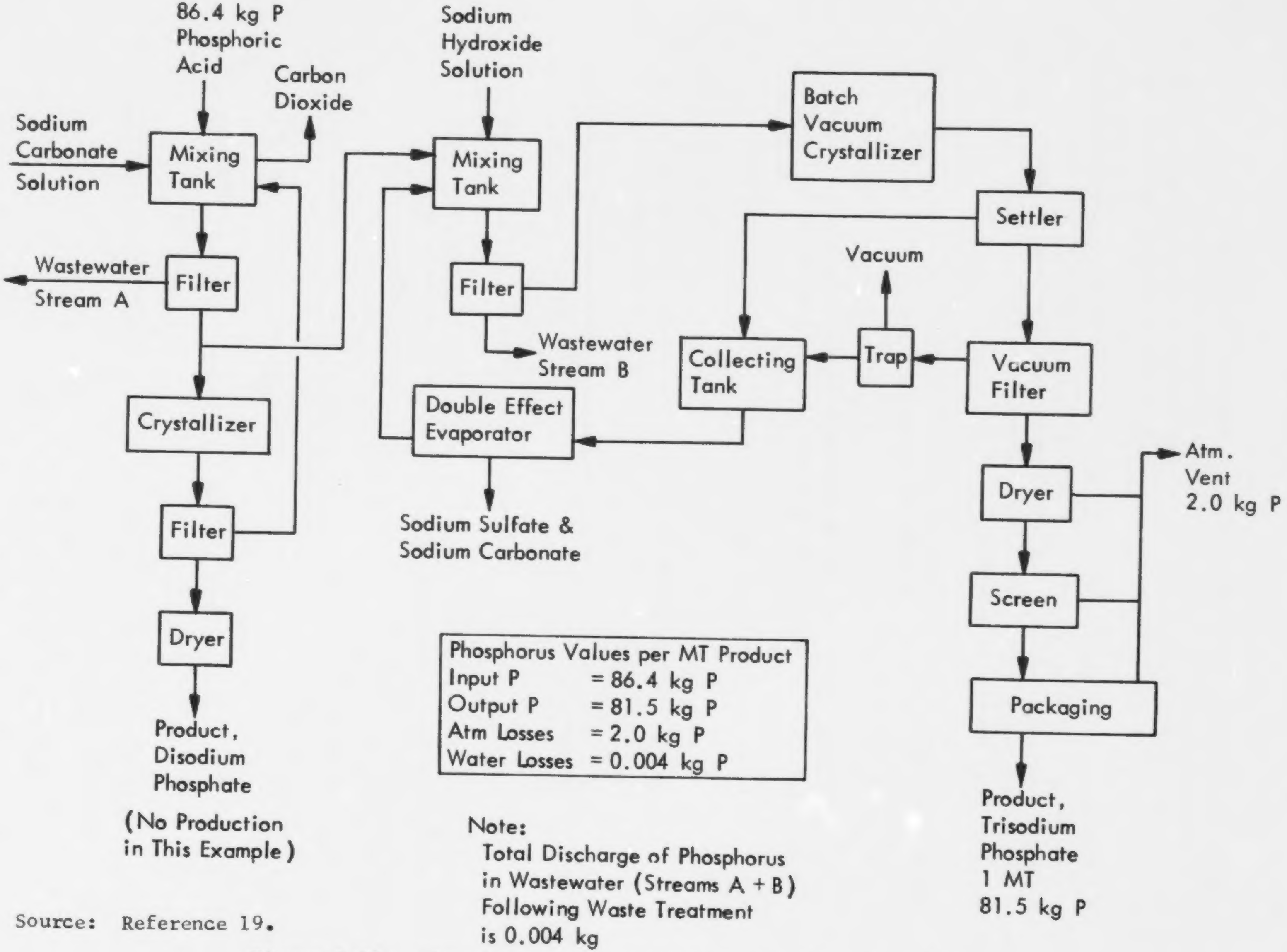
$$Na_2HPO_4 + NaOH \longrightarrow Na_3PO_4 + H_2O$$

Material balance data--[12] The quantities of reactants are based on 1 MT trisodium phosphate, $Na_3PO_4 \cdot 12\ H_2O$ as follows:

	Kilograms	Phosphorus content (kg)	Product	Kilograms	Phosphorus content (kg)
Phosphoric acid (45% P_2O_5)	440	86.4	TSP ($Na_3PO_4 \cdot 12\ H_2O$)	1,000	81.5
Sodium carbonate (58% Na_2O)	300	0			
Sodium hydroxide (76% Na_2O)	120	0			

A phosphorus mass balance showing values which apply for 1 MT of sodium phosphate product is:

Input		
Phosphoric acid	86.4 kg P	
Outputs		
Product	81.5 kg P	
Total wastewater losses	0.004 kg P	Total P losses, 2.004 kg P
Total atmospheric losses	2.0 kg P	
Unaccounted for P	2.896 kg P	


86.4 kg P
Phosphoric
Acid
Carbon
Dioxide
Sodium
Carbonate
Solution
Mixing
Tank
Filter
Wastewater
Stream A
Crystallizer
Filter
Dryer
Product,
Disodium
Phosphate
(No Production
in This Example)
Sodium
Hydroxide
Solution
Mixing
Tank
Filter
Wastewater
Stream B
Double Effect
Evaporator
Sodium Sulfate &
Sodium Carbonate
Batch
Vacuum
Crystallizer
Settler
Vacuum
Collecting
Tank
Trap
Vacuum
Filter
Dryer
Atm.
Vent
2.0 kg P
Screen
Packaging
Product,
Trisodium
Phosphate
1 MT
81.5 kg P
Phosphorus Values per MT Product
Input P = 86.4 kg P
Output P = 81.5 kg P
Atm Losses = 2.0 kg P
Water Losses = 0.004 kg P
Note:
Total Discharge of Phosphorus
in Wastewater (Streams A + B)
Following Waste Treatment
is 0.004 kg

Source: Reference 19.

Figure 6-18. Flow diagram for production of sodium phosphates.

Wastewater effluent--The range of raw wastewater discharged by sodium phosphate plants varies from 7,640 to 10,013 liters/MT product.[18] Since a typical effluent contains about 250 mg of total phosphorus per liter, the total phosphorus content of the raw wastewater ranges from 1.9 to 2.5 kg/MT product.

The EPA recommendation of effluent limitation guidelines (BPCTCA) for the sodium phosphates subcategory show that the maximum phosphorus discharge should not exceed an average of 0.004 kg of total phosphorus for each metric ton of product.[20] It is assumed that the treated wastewater discharged to the environment contains this amount of phosphorus.

Atmospheric emissions--The process operations of product drying, cooling, grinding, and packaging are considered to be significant sources of air emissions of product particulates.

Estimates of the phosphorus emissions to the atmosphere were based on published data.[5] These estimates are according to methods described earlier in this section (see page 98); the results are shown in Table 6-10. The estimated total phosphorus discharge to the atmosphere is 2.0 kg phosphorus per metric ton product.

TABLE 6-10. SOURCES AND ESTIMATES OF PHOSPHORUS-CONTAINING AIR EMISSIONS FOR SODIUM PHOSPHATES (EXCLUDING SODIUM TRIPOLYPHOSPHATE)

Production activity	Uncontrolled particulate emission factor (kg/MT)	% P_2O_5 in emissions	Estimated level of emission control (%)	P emissions after controls (kg P/MT product)
Drying-cooling	30	a/	90	1.3
Grinding	10	a/	97	0.1
Bagging	0.5 b/	a/	b/	0.2
Material handling	1	a/	0	0.4
Total				2.0

a/ Emission factor includes % P_2O_5.

b/ Emission factor after control.

Source: Reference 5.

National emission for production of sodium phosphates--For all other sodium phosphate products except STPP, the estimated national production rate in 1978 is 353,000 MT (Table 6-17). The annual discharge of phosphorus can be estimated at 1 MT for wastewater and 706 MT for air emissions.

Production of Food-Grade Calcium Phosphates (SIC No. 2819)--

These products are made by the neutralization of phosphoric acid (furnace process) with lime.[19] Integrated plants producing all types of calcium phosphate products are common in the industry. The reactions are chemically similar; however, the methods of manufacturing the various calcium phosphates differ substantially from one another in the amount and type of lime used and the quantity of process water required. The standard flow diagram for these products is shown in Figure 6-19, and detailed information on these processes is presented in References 11 and 19.

Monocalcium phosphate (MCP) production--A relatively pure MCP is prepared in a stirred batch reactor from furnace phosphoric acid and lime slurry according to the reaction:[19]

$$2H_3PO_4 + Ca(OH)_2 \longrightarrow Ca(H_2PO_4)_2 \cdot H_2O + H_2O$$

An excess of phosphoric acid is maintained during the batch reaction cycle to inhibit formation of dicalcium phosphate. A minimum amount of process water is used.[19]

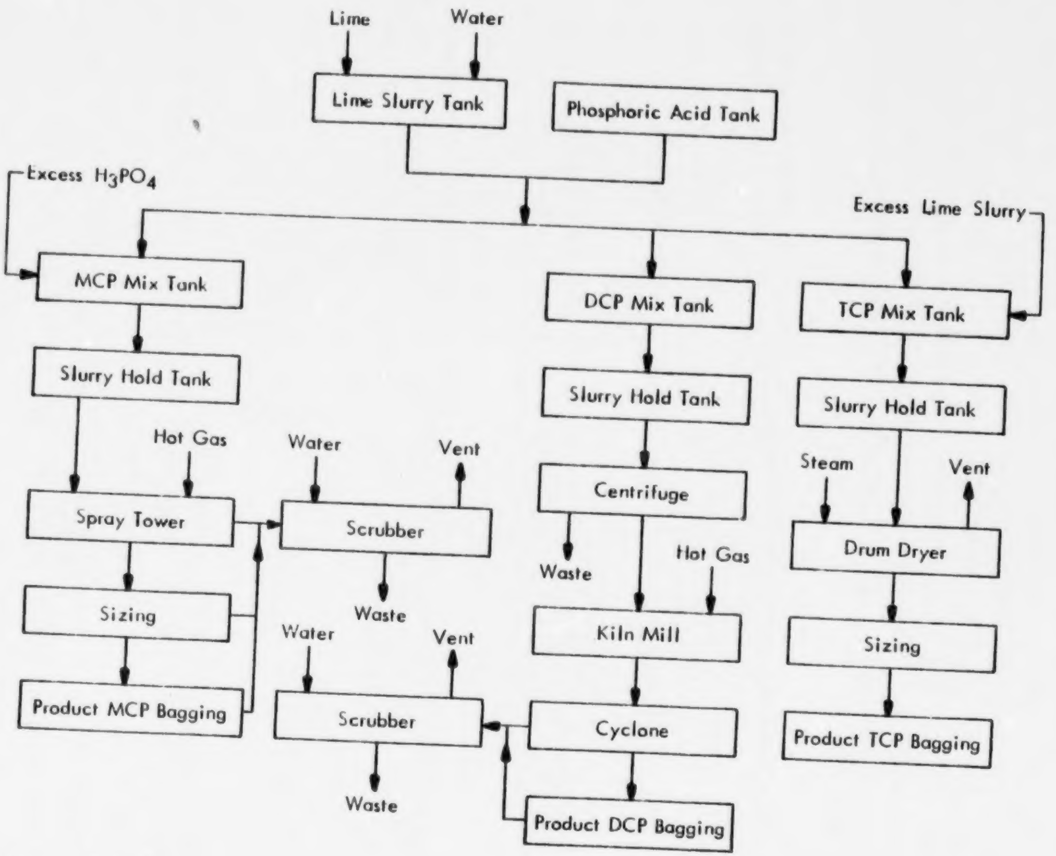
Tricalcium phosphate (TCP) production--TCP is prepared in a manner similar to that for MCP, except that an excess of lime slurry is maintained during the batch reaction to inhibit formation of dicalcium phosphate.[19] The reaction is:

$$2H_3PO_4 + 3Ca(OH)_2 \longrightarrow Ca_3(PO_4)_2 + 6H_2O$$

Dicalcium phosphate (DCP) production--This product is prepared using batch reactors with much more process water than for MCP or TCP production.[19] The reaction is:

$$H_3PO_4 + Ca(OH)_2 \longrightarrow CaHPO_4 \cdot 2H_2O$$

Wastewater effluent--The raw wastewater from production of food-grade calcium phosphates is from two primary and approximately equal sources: filtrate from dewatering of DCP slurry and effluent from wet-scrubbers, which collect airborne solids from product drying operations. Both sources contain finely divided, suspended particles of calcium phosphates.[19]


Lime
Water
Lime Slurry Tank
Phosphoric Acid Tank
Excess H_3PO_4
Excess Lime Slurry
MCP Mix Tank
DCP Mix Tank
TCP Mix Tank
Slurry Hold Tank
Slurry Hold Tank
Slurry Hold Tank
Hot Gas
Water
Vent
Steam
Vent
Spray Tower
Scrubber
Centrifuge
Drum Dryer
Waste
Hot Gas
Sizing
Waste
Water
Vent
Kiln Mill
Sizing
Product MCP Bagging
Scrubber
Cyclone
Product TCP Bagging
Waste
Product DCP Bagging

Source: Ref. 19

Figure 6-19. General flow diagram for production of food-grade calcium phosphates.

In an integrated plant, the normal practice is to partially recycle the scrubber water and to partially use the DCP filtrate as makeup scrubber water. The total raw wastes from this system are typically 4,200 liters/MT product; these wastes contain 100 kg/MT of solids (amounting to a concentration of 2.4% by weight).[19] In addition, 30 kg/MT of dissolved solids originate from the phosphoric acid mists in the scrubbers and from excess phosphoric acid in the reaction slurry for the MCP process.[19] A summary of the phosphorus-containing raw wastes from food-grade calcium phosphate plants is given in Table 6-11.

TABLE 6-11. SUMMARY OF PHOSPHORUS-BEARING RAW WASTES FROM FOOD-GRADE CALCIUM PHOSPHATE PLANTS

	Dewatering	Solids scrubbing	Total
Process water wasted: (liter/MT product)	2,100	2,100	4,200
Raw waste load, dissolved PO_4 (kg/MT product)	15	15	30
Solid wastes (kg/MT product)		10	10

Source: Ref. 19

The EPA recommended effluent limitations (BPCTCA) for food-grade calcium phosphates is a maximum average discharge (for 30 consecutive days) of 0.17 kg total phosphorus per metric ton of product manufactured.[20]

Atmospheric emissions--Emissions which occur during processing were estimated on the basis of published data[5] and on calculation methods described earlier in this section. A summary of the estimated emission values is given in Table 6-12. The estimated total air emissions are 2.3 kg phosphorus per metric ton MCP or TCP product and 2.4 kg phosphorus per metric ton DCP product.

Summary of phosphorus discharges to environment--Data on phosphorus discharges to the environment which apply for 1 MT of food-grade calcium phosphate follows:

MCP or TCP production

$$\left.\begin{array}{ll}\text{Total wastewater losses} & 0.17\text{ kg P}\\ \text{Total atmospheric losses} & 2.30\text{ kg P}\end{array}\right\}\text{ Total P losses, 2.47 kg}$$

TABLE 6-12. SOURCES AND ESTIMATES OF PHOSPHORUS-CONTAINING AIR EMISSIONS FOR FOOD-GRADE CALCIUM PHOSPHATES

Production activity	Uncontrolled particulate emission factor (kg/MT)	% P_2O_5 in emissions	Estimated level of emission control (%)	P emissions after controls (kg P/MT product)
MCP or TCP production				
Drying-cooling	30	a/	90	1.3
Bagging	0.5 b/	a/	NA	0.2
Material handling (total)	2	a/	NA	0.8
Total				2.3
DCP production				
Drying-cooling	30	a/	90	1.3
Grinding	10	a/	97	0.1
Bagging	0.5 b/	a/	NA	0.2
Material handling (total)	2	a/	NA	0.8
Total				2.4

Source: Ref. 5.

a/ Emission factor includes % P_2O_5.

b/ Emission factor after control.

NA = Not available.

DCP production

Total wastewater losses	0.17 kg P	Total P losses, 2.57 kg P
Total atmospheric losses	2.40 kg P	

National emission for production of food-grade calcium phosphates--The total domestic production of these products for 1978 is about 51,000 MT. Using the emission factors shown in Table 6-17, the total annual losses of phosphorus to the environment from these processes are calculated to be 9 MT from discharged wastewater and 122 MT from air emissions.

Production of Laundry Detergents (SIC No. 2841)--

Two basic types of detergent products are spray dried materials and liquid detergents. The process technology involved in the manufacture of these products is described in Reference 22. A wide variety of raw materials can be used in these manufacturing operations. Detergents can be formulated with different inorganic and organic chemicals to provide the same cleaning power and have the same biodegradability. They can also be formulated to:

Maximize cleaning power.

Maximize biodegradability.

Minimize eutrophication potential in a specific receiving water.

Maximize cleaning power per unit of cost.

Minimize air or water pollutants and solid wastes generated by the production process.

Although detergent companies and their suppliers have expended a significant research and development effort to develop substitutes for phosphates in detergent products, no replacement has been found which is both effective, and competitive on a basis of production cost.22/ Manufacturers are generally reformulating with lower concentrations of phosphate, substituting nonionic for anionic organic surfactants, and using additional amounts of alkaline builders such as sodium silicates and sodium carbonates.

Spray dried products are reported to represent the largest volume unit process utilized by the soap and detergent industry.22/ The principal sources of contaminated water are washdown of the drying tower, water discharged from off-gas scrubbers, and leaks and spills. A very small quantity of particulate waste material is vented to the atmosphere. All waste streams are contaminated with the detergent being produced.

The manufacture of liquid light-duty dishwashing and heavy-duty laundry detergents is conducted in relatively simple equipment for blending of the various ingredients.[22] Contaminated effluent is produced by leaks and spills from the product filling line. In both the blending and filling activities, purging of the process line between batch product runs produces discharges of detergent contaminated water. Also, filled detergent bottles are sometimes washed which results in additional wastewater.

The contaminants in waste effluents from the processing of light-duty liquid products are very high in surface active agents.[22] The operations conducted for heavy-duty liquid detergents can also result in some wastewater contamination with builders such as phosphates and carbonates.

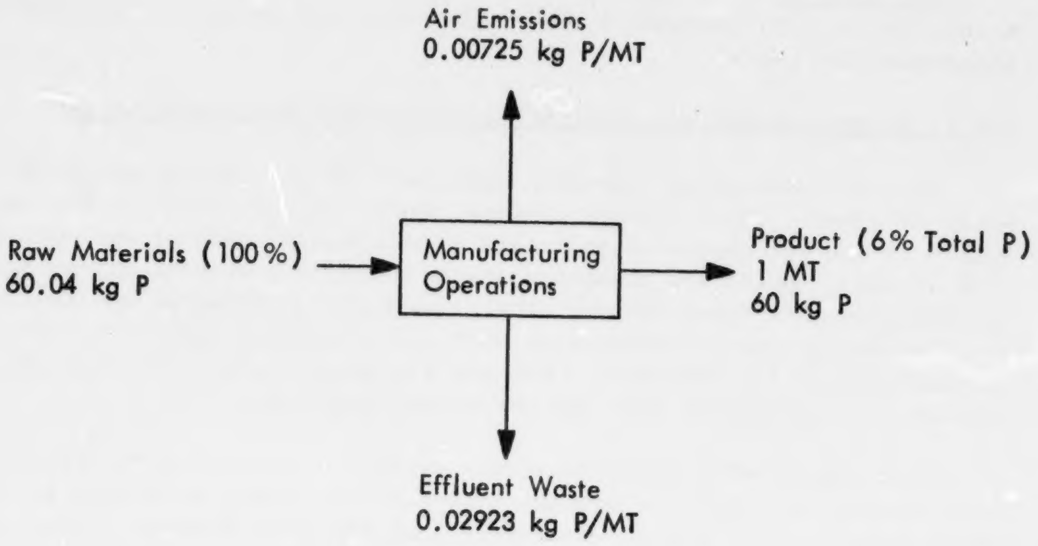
Phosphate levels found in the raw wastewaters and treated effluents from plants producing soaps and detergents are reported to be comparable to those encountered in the influents and effluents of well operated municipal treatment plants. In 1973, more than 95% of the plant effluents were being discharged to municipal treatment plants.[22]

Information on a representative process flow diagram for the domestic production of phosphorus-based laundry detergents by one U.S. producer was obtained by telephone contacts with a company spokesman. This information is presented in Figure 6-20. Attempts to obtain similar process data from other domestic producers were unsuccessful.

Material balance data--A phosphorus mass balance showing values which apply for 1 MT of laundry detergent product follows:

Input	60.04 kg P	
Outputs		
Product	60 kg P	
Total wastewater losses	0.02923 kg P	Total P losses, 0.03648 kg
Total atmospheric losses	0.00725 kg P	
Unaccounted for P	0.00352 kg	

National emission for production of phosphorus-based laundry detergents--The estimated domestic production of these products in 1978 is 1,860,000 MT (Table 6-17). The total annual phosphorus discharges from these processes can be estimated, using the emission factors in Table 6-17, to be 54 MT in discharged wastewater and 13 MT in air emissions.



Source: Industry contacts.

Figure 6-20. Flow diagram for production of laundry detergent.

Metal Surface Treatment--

Phosphoric acid is used domestically in various treatment operations (phosphoric acid baths) for plating and polishing of metal surfaces.[5] Dry-process phosphoric acid is generally used. Four important applications are: (a) phosphating or forming a protective coating of an insoluble phosphate salt; (b) polishing and brightening metal surfaces; (c) electropolishing in phosphoric acid baths; and (d) chemical plating of a nickel-phosphorus alloy on various surfaces. All of these operations emit phosphoric acid mist into the atmosphere.

Information obtained from industry spokemen indicate that the total phosphorus consumption as phosphoric acid for acid treatment of metal surfaces will be about 34,000 MT of contained phosphorus in 1978.

Wastewater--Based on information provided by a supplier of phosphoric acid, it was assumed that wastewater containing phosphorus is treated to control pollution and that the maximum discharged phosphorus rate is equivalent to the standard (0.044 kg phosphorus per metric ton of acid) which applies for production of dry-process phosphoric acid (Pacheco, J., Personal Communication, FMC Corporation, Philadelphia, Pa., November 1, 1978). On this basis, the estimated total phosphorus discharge in wastewater is 10 MT phosphorus per year.

Air emission--The reported controlled emission rate is 0.12 kg P_2O_5 per metric ton of acid consumed.[5] The estimated total phosphorus emission is 27 MT phosphorus per year.

Use of Phosphorus-Derived Chemicals in Industrial Water Treatment--

In industrial water treatment operations (e.g., cooling water, boiler water treatment, etc.) various chemical agents must be added to the water system to control corrosion and scaling problems.[23] Some of the most effective chemical agents are phosphorus-based materials, such as polyphosphates and phosphonates. Other control chemicals, such as chromates and zinc compounds, are frequently used in combination with the phosphorus chemicals. The use of these chemicals is considered necessary for proper water treatment and to ensure against lost production time and excessive energy use.

Heat generated in many industrial processes is usually dissipated by a water-cooled heat transfer system. In industrial plants utilizing an open recirculating cooling system, warm water from the heat transfer system is pumped to a cooling tower. During passage over the cooling tower, the evaporation of some water serves to cool the remaining water.[23] If required, additional water is added and the cooled water is recycled to the heat source. As the water recycling process continues, minerals initially present in the water will concentrate and, if remedial action is not taken, these minerals will eventually precipitate as scale-forming salts (e.g., calcium carbonate and calcium sulfate) on heat transfer surfaces. This scale reduces cooling efficiency and eventually requires the system to be shutdown for cleaning.

As the water is passed over the cooling tower, two other processes also occur. First, particulates are scrubbed from the air and these particles can deposit on metal surfaces to cause fouling. Secondly, during aeration the water becomes saturated with oxygen which increases the electrolytic corrosive action of the water.[23] The corrosion action results in the deposition of oxides on the metal surfaces. These coatings will impede heat transfer or reduce water flow resulting in decreased cooling efficiency.

Effective corrosion control has been accomplished for over 20 years using a combination of 10 to 20 ppm chromate compounds, 3 to 10 ppm phosphates, and 1 to 3 ppm zinc compounds. This combination allows cooling system operations to utilize mild steel equipment, which is adequately protected by these chemicals rather than corrosion-resistant metals.

Because of stringent water quality standards for metals in several states, water treatment companies have been conducting research to develop nonmetallic corrosion inhibitors. These nonmetallic agents (e.g., polyphosphates, such as sodium tripolyphosphate) are now available and provide acceptable control of corrosion and deposition in some industries. However, the use of phosphate and other phosphorus-containing chemicals is also required in each of these newer approaches (Weidman, J. G., Personal Communication, Betz Laboratories, Trevose, Pennsylvania, January 1978).

Phosphate additives are also used extensively for boiler water treating. Cost effective and energy effective alternatives to the use of phosphorus compounds appear to be unavailable for boiler water treating as well as for cooling water service (Tuckett, W. F., Personal Communication, Phillips Petroleum Company, Bartlesville, Oklahoma, January 1978).

Another important use of phosphorus-based deposit control agents is to prevent deposition in gas scrubbers (Weidman, J. G., Personal Communication, Betz Laboratories, Trevose, Pennsylvania, January 1978). Under the Clear Air Act, the EPA has established emission standards for many industry categories which can only be met by efficiently operating gas scrubbers. If deposition occurs, the plants must be shutdown or the scrubbers bypassed for cleaning. When the units are bypassed, the operator risks being in violation of the Act.

Attempts to obtain a definitive breakdown of the percentage of water treatment phosphorus chemicals in wastewater actually discharged to publicly owned treatment works were unsuccessful.

National emission for use of water treatment chemicals--Attempts to obtain representative flow diagrams and phosphorus material balance data for domestic water treatment systems were unsuccessful. The approximate quantity of phosphorus-based chemicals used domestically for water treatment in 1978 is reported to represent from 18,140 to 27,210 MT (40 to 60 million pounds) of contained phosphorus, or about 0.8 to 1.5% of total domestic phosphorus consumption (Weidman, J. G., Personal Communication, Betz Laboratories, Trevose, Pennsylvania, January 1978). With the assumption that 50 million pounds of phosphorus is annually discharged to the environment, an estimated 22,700 MT were released in 1978.

Domestic Sewage--

The National Commission on Water Quality (NCWQ) has reported that the daily total flow from publicly owned sewage treatment plants during 1973 was about 91 million cubic meters (24,000 million gallons) and that the total phosphorus load in this effluent was about 800 MT (880 tons).[24] Converting these values to concentration (mass of total phosphorus divided by effluent volume) one finds that the phosphorus concentration in sewage treatment plant effluents for 1973 was about 8.8 mg/liter.

The 1976 Needs Survey indicates that the total nationwide volume of sewage collected daily in 1975 was 96,662,000 m^3 (25,500 million gallons).[25] If it is assumed that all sewage collected was discharged as treated wastewater and that the average concentration of 8.8 mg/liter of phosphorus did not change, then the total phosphorus emitted from publicly owned sewage treatment plants in 1975 was 850 MT/day (935 tons/

day). This quantity of phosphorus represents domestic, commercial, and industrial contributors.

When the 1976 daily phosphorus loads are multiplied by 365, an estimated 310,000 MT (340,000 tons) of total phosphorus were discharged annually by the sewage treatment plants. Using the population of 157,434,000 persons served by publicly owned sewage treatment plants as reported in the 1976 Needs Survey, this quantity becomes 2.15 kg (4.7 lb) of phosphorus being discharged per person per year.

An overall total (household, industry, and institution) of 1.63 kg phosphorus per person per year is charged into sewage treatment systems. (Fealey, T. Personal communication. Proctor and Gamble Company, Cincinnati, Ohio.) Thus, there is a discrepancy between the quantity of phosphorus that has been estimated to be contributed to the sewage treatment plant (1.63 kg) and that which has been estimated to be discharged from the plant after treatment (2.15 kg). It is believed that the source of this discrepancy lies in an underestimation of the phosphorus discharged by industrial and commercial sources. Quantities of phosphorus from commercial and industrial sources can be better estimated by determining differences between total phosphorus contributed and phosphorus from domestic/household sources.

From the average annual per capita phosphorus loads indicated in Table 5-4 (0.68 kg from laundry detergent, 0.47 kg from human waste, and 0.20 kg from miscellaneous sources; total of 1.35 kg per capita are used), it can be calculated that the 157,434,000 persons served by publicly owned sewage treatment plants will contribute 213,000 MT (234,000 tons) of phosphorus to sewage treatment facilities annually. This contribution of phosphorus to sewage treatment plants from domestic/household sources is only part of the total load; additional phosphorus is added from commercial establishments and industry.

Typical concentrations of total phosphorus in influent to sewage treatment plants are shown in Table 6-13. The average phosphorus concentration is 10.6 mg/liter with a standard deviation of 3.6 mg/liter. Using the 10.6 mg/liter value as the representative average concentration of total phosphorus in influent and a total daily flow of 96.6×10^9 liters, the total phosphorus load to sewage treatment plants is 374,000 MT/year (412,000 tons/year). Thus the difference between total phosphorus load and domestic/household load is the quantity of phosphorus contributed to sewage treatment plants by commercial and industrial establishments annually, i.e., 161,000 MT/year (178,000 tons/year). Thus, domestic/household sources contribute about 57% of the total influent load, and commercial industrial sources account for the other 43%. The large percentage of phosphorus from commercial and industrial sources is believed to be due to usage of phosphorus-containing cleaning compounds in industrial plants and commercial establishments such as restaurants, laundries, hotels, car washes, filling stations, etc.

TABLE 6-13. TYPICAL CONCENTRATIONS OF TOTAL PHOSPHORUS IN RAW SEWAGE AT VARIOUS LOCATIONS

Location	Total P in raw sewage (mg/ℓ)
Grayling, MI	10-20
Benton Harbor, MI	7.6
Trenton, MI	11.7
Waukegan, IL	8.2
Pontiac, MI	7.5
Michigan City, IN	10
Babbitt, MN	11
Dogue Creek STP, VA	9.0
Little Hunting Creek STP, VA	10
Rochester, NY	8
Seneca Falls, NY	6.3
Richardson, TX	11.4
Chapel Hill, NC	11.3
Wyoming, MI	10.4-17.5

Source: Adapted from data contained in Ref. 26.

As discussed earlier, the annual quantity of phosphorus estimated to be discharged from all of the sewage treatment plants is 310,000 MT/year; the phosphorus input estimate is 374,000 MT/year. Thus, one a nationwide basis, the average reduction of phosphorus during sewage treatment is 64,000 MT/year, or about 17%. If it is assumed that sewage treatment reduces phosphorus independent of source, then one finds that phosphorus coming from domestic/household sources in treated wastewater is about 177,000 MT/year, while that from commercial and industrial sources is approximately 133,000 MT/year as shown in Table 6-14.

As stated above, it is estimated that nationwide sewage treatment removes an average of about 17% of the phosphorus present in the input sewage. This percentage represents the cumulative effect of the various types of sewage treatment processes on the degree of phosphorus removal, typical values of which are shown in Table 6-15. Primary treatment is relatively ineffective towards phosphorus removal. Secondary treatment will remove 10 to 20% of the phosphorus; however, addition of chemicals specifically for phosphorus removal can reduce levels considerably (by 80 to 95%).

TABLE 6-14. SOURCES OF PHOSPHORUS LOADING IN TREATED EFFLUENT FROM MUNICIPAL SEWAGE TREATMENT PLANTS

Phosphorus source	Phosphorus discharged in treated effluent (MT/year)	%
Domestic/household:		
Laundry detergent	75,000	24.2
Automatic dishwashers	13,000	4.2
Personal sewage	71,000	22.9
Garbage disposals	18,000	5.8
Total domestic/household	177,000	57.1
Commercial/industrial	133,000	42.9
Nationwide total	310,000	100.0

TABLE 6-15. EFFECTIVENESS OF PRIMARY AND SECONDARY TREATMENT PROCESSES ON PHOSPHORUS REMOVAL WITH AND WITHOUT CHEMICAL ADDITION

	Percent removal					
	Phosphorus		Suspended solids		BOD	
Treatment	Without	With	Without	With	Without	With
Primary treatment	5-10	70-90	40-70	60-75	25-40	40-50
Secondary treatment:						
Trickling filter	10-20	80-95	70-92	85-95	80-90	80-95
Activated sludge	10-20	80-95	85-95	85-95	85-95	85-95

Source: Ref. 26.

Unfortunately, the number and location of plants employing chemical addition for phosphorus removal is not readily available. Therefore, in order to estimate the phosphorus emissions from publicly owned sewage treatment plants on a regional basis, the nationwide value of 17% was used to estimate average percent phosphorus removal from the three types of sewage treatment listed in the 1976 Needs Survey.25/ The procedure for estimating regional quantities of phosphorus removal is discussed in the following paragraphs.

In the 1976 Needs Survey,[25] the population (157,434,000) served by various levels of sewage treatment has been broken down by states; this population represents 72.6% of the nation's population. The percentage has been further broken down into types of sewage treatment used. Nationwide, 18.6% of the population is served by less than secondary treatment (assumed to be primary treatment), 15.0% by secondary treatment, and 21.1% by tertiary treatment.[25] Because of the manner in which population data were gathered and interpreted, the total percentage of the population served by municipal sewage treatment plants is only 54.7% rather than 72.6%. Thus, there is some discrepancy in the information concerning the distribution of sewage treatment processes in the country; this discrepancy is acknowledged and explained in the Needs Survey.

The 1976 Needs Survey used the term "tertiary treatment" to mean removal of BOD (biological oxygen demand) and suspended solids to levels which are less than those found in secondary treatment effluent. Thus, phosphorus removal per se is not a part of the Needs Survey definition of tertiary treatment. However, some phosphorus removal would be expected in treatment plants which produce effluent of better quality than secondary treatment. From data in Table 6-15 for phosphorus removal in primary (average 7% removal) and secondary (average 15% removal) treatment, and the volume data for primary and secondary treatment as reported in the Needs Survey, it was possible to estimate the fraction of the 310,000 MT/year of phosphorus emitted in effluent from these types of plants. The remaining phosphorus tonnage was assumed to be emitted from plants with tertiary treatment. Using these data to estimate a phosphorus concentration in the effluent and comparing this estimate with the 10.6 mg/liter in the influent (see p. 149), a value of about 35% phosphorus removal is obtained from wastewaters undergoing tertiary treatment. Thus, on a nationwide basis, the average values of phosphorus removal by various categories of treatment processes are:

Treatment category	Phosphorus removal (%)
Less than secondary (primary)	7
Secondary	15
Tertiary	35

Using these assumptions, formulae for estimating phosphorus emissions from publicly owned sewage treatment plants due to domestic/household and commercial/industrial sources have been developed. The formulae are:

- Domestic/household:

$$\text{pop} \times 1.35 \times \left[\frac{(0.93 \times \%\ \text{Pri}) + (0.85 \times \%\ \text{Sec}) + (0.65 \times \%\ \text{Ter})}{(\%\ \text{Pri} + \%\ \text{Sec} + \%\ \text{Ter})}\right]$$

$$\times\ 0.001 = P_d$$

where: Pop = population (Table 3, 1976 Needs Survey),[25]

1.35 = kg P contributed per capita per year,

% Pri = percent of population receiving primary sewage treatment (Table 3A, 1976 Needs Survey),[25]

% Sec = percent of population receiving secondary treatment (Table 3B, 1976 Needs Survey),[25]

% Ter = percent of population receiving tertiary treatment (Table 3C, 1976 Needs Survey),[25]

0.001 = conversion factor for kg to MT, and

P_d = total phosphorus discharged after treatment from domestic/household sources, MT/year.

- Commercial/industrial:

$$(\text{Total flow}) - (\text{Pop} \times 380) \quad \times 365 \times 12.0 \times$$

$$\left[\frac{(0.93 \times \%\ \text{Pri}) + (0.85 \times \%\ \text{Sec}) + (0.65 \times \%\ \text{Ter})}{(\%\ \text{Pri} + \%\ \text{Sec} + \%\ \text{Ter})}\right]$$

$$\times\ 10^{-9} = P_c$$

where: Total flow = average daily flow in liters/day (Table 15, 1976 Needs Survey),[25]

Pop = population served (Table 3, 1976 Needs Survey),[25]

380 = volume (liters) of water contributed per person per day,

365 = days in a year,

12.0 = concentration (mg/liters) of phosphorus in commercial/industrial influent,*

% Pri = as defined above,

% Sec = as defined above,

% Ter = as defined above,

10^{-9} = conversion factor for mg to MT, and

P_c = total phosphorus discharged after treatment from commercial/industrial sources, MT/year.

Using these formulae, the estimates for 1975 and for 1978 arranged according to region are presented in Table 6-16. In addition to the assumptions already discussed, the estimates assume that the fraction of the commercial/industrial phosphorus load to the sewage treatment plant is distributed in the same way as for the domestic/household phosphorus. In addition, the estimates do not reflect the banning of phosphate in detergents in certain states or particularly stringent state effluent standards. Nationwide phosphorus values in Table 6-16 do not add up to totals estimated earlier because of rounding errors, and the use of "average phosphorus removal for the three types of sewage treatment. Also, contributions from outlying areas, e.g., Puerto Rico, the Virgin Islands, Guam, American Samoa, and Pacific Trust Territories, have not been included.

The preceding discussion has been based on information relating to the country's population served by municipal treatment plants. This population is only 70% of the total. The remaining 30% represents persons who do not contribute to municipal sewage treatment plants, and presumably

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* The value of 12.0 mg/liter phosphorus input to sewage treatment plants was established in the following manner. Annual phosphorus contribution from commercial/industrial sources is estimated to be 161,000 MT/year, or about 440 MT/day (see p. 149). The total daily volume of collected sewage is 96.66×10^9 liters, of which 59.82×10^9 liters come from domestic/household sources using the rule of thumb value of 380 liters/day (100 gal/day) and 157,434,000 persons. Thus, the daily volume of sewage to publicly owned treatment plants is 36.84×10^9 liters/day. From daily loads of phosphorus (440 MT) and daily volumes (36.84×10^9 liters), one calculates that the average concentration of phosphorus in influent from commercial/industrial sources is 12.0 mg/liter.

TABLE 6-16. PHOSPHORUS LOAD ESTIMATES FOR MUNICIPAL SEWAGE TREATMENT PLANTS

	Estimates for 1975 Treatment plant effluent, MT of total P/year			Estimates for 1978[a] Treatment plant effluent, MT of total P/year		
U.S. region[a]	P, domestic and household	P, commercial and industrial	Total P	P, domestic and household	P, commercial and industrial	Total P
Northeast	5,416	7,717	13,133	6,149	7,863	14,012
Middle Atlantic	35,351	26,656	62,007	36,506	26,793	63,299
South Atlantic	21,813	13,086	34,899	23,928	13,874	37,802
East North Central	34,369	41,322	75,691	32,851	41,604	74,455
East South Central	7,396	11,380	18,766	8,309	10,716	19,025
West North Central	15,535	7,595	23,130	16,276	8,644	24,920
West South Central	15,207	4,586	19,793	16,666	6,301	22,967
Mountain	8,194	5,225	13,419	9,073	5,598	14,671
Pacific	25,981	9,977	35,958	27,522	11,579	39,101
Total United States (rounded to nearest 1,000 MT)	169,000	128,000	297,000	177,000	133,000	310,000

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[a] A table showing the state-by-state loading estimates for 1978 is given in Appendix B.

use septic tanks or small community lagoons for sewage treatment. Baseline information for effectiveness of these treatment systems in terms of phosphorus removal is lacking, and therefore no estimates have been made. In the case of septic tank treatment, phosphorus loads are likely to be small. It is generally assumed that practically all phosphorus is removed from water treated by soil in a septic tank system. However, in certain cases where soils are excessively sandy, it is questionable whether this assumption is valid.

The procedures developed for the 1975 estimates of state and regional phosphorus emissions from publicly owned municipal treatment plants have been used for the 1978 estimates. The differences between the 1975 data and the 1990 projections in the Needs Survey have been linearly extrapolated to 1978 population served by municipal treatment plants, flows collected, and percent of plants with primary, secondary, and tertiary treatment. In addition, the EPA has developed an estimate of the publicly owned treatment plants which will require phosphorus removal by 1990. (Memos: J. Yance to J. Welch, OTS; 9/9/78, 9/1/78.) Thus, the assumption was made that these plants did not have phosphorus removal capability in 1975, but that some progress had been made between 1975 and 1978 to achieve the needed phosphorus removal. The 3 years of progress were assumed to have achieved 20% of the 15-year goals (i.e., the 1990 goals for phosphorus removal).

The results of these calculations based upon the aforementioned extrapolation and assumption are shown in Table 6-16. In general, there is a little more phosphorus being discharged in 1978 from publicly owned sewage treatment plants than was the case in 1975. This greater quantity is not due to less efficient treatment; rather, it is due to the increased population served and the increased capacity of publicly owned sewage treatment plants.

This trend is also seen when the 1990 projections in the 1976 Needs Survey are used to project phosphorus emissions in 1990. The nationwide estimates for phosphorus emissions for 1975, 1978, and 1990 are summarized below.

Source	1975 MT/year	1978 MT/year	1990 MT/year
Domestic/household	169,000	177,000	193,000
Commercial/industrial	128,000	133,000	148,000
Total	297,000	310,000	341,000

Inadvertent Point Sources--

The estimated national phosphorus emissions from inadvertent point sources for 1973 were taken from the literature.[4] This information was updated by adjusting the emission levels according to reported changes in the respective production or consumption rates for each source between 1973 and 1978. For example, it was estimated that the national production rate for iron increased by about 7% over this period. Thus, the 1973 emission rate of 2,800 MT/year was increased by this percentage (2,800 x 1.07) to obtain a value of 3,000 MT of phosphorus discharged in 1978.

A tabular summary of all estimated national point sources, including inadvertent sources, is shown in Table 6-17.

Conclusions for National Assessments

A summary of the estimated national phosphorus discharges to the environment for 1978 is presented in Table 6-18.

The aggregate of the nonpoint source discharges accounts for 87.6% of the total estimated national emissions of about 2.9 million metric tons of phosphorus. The major contributors in this category are cropland and runoff (~ 49%) and pasture and rangeland (~ 34%). About 99% of the total phosphorus discharges from nonpoint sources comes from runoff water with the balance attributable to air emissions from inadvertent sources.

In contrast to the nonpoint source discharges, the estimated aggregate point source phosphorus discharge accounts for only 12.4% of the total national emissions. The phosphorus loading in municipal sewage treatment effluent accounts for the bulk (10.6%) of the discharges in the point source category. The total air emissions from point sources account for about 55% of the national total air emissions and the quantity of identified phosphorus in solid wastes (32 MT phosphorus per year) is negligible.

The top 10 ranking of factors in descending order of importance (in terms of magnitude of phosphorus emissions) on a national level are shown on p. 161.

TABLE 6-17. ESTIMATED NATIONAL POINT SOURCE DISCHARGES OF TOTAL PHOSPHORUS TO THE ENVIRONMENT IN 1978

SIC No.	Industry or activity description	Product manufacturing rate			Discharges to environment					
					Discharged wastewater		Air emissions			
		Base data for year ( ) 10^3 MT/Yr	Extrapolation factor or comment	Estimate for 1978 10^3 MT/Yr	Emission factor kg P/MT product	MT of phosphorus	Emission factor kg P/MT product	MT of phosphorus	Solid wastes, MT of phosphorus	Total discharge MT of phosphorus
1475	A. Phosphate rock mining and beneficiation									
	Eastern operations	-	-	44,306	0.0050	222	0.094	4,165	0	4,387
	Western operations	-	-	6,042	0	0	0.180	1,100	0	1,100
	A. subtotal	44,452 (1976)a/	1.064/yra/	50,348	-	222	-	5,265	0	5,487
	B. Agricultural consumption of phosphate rock - manufacturing operations									
2874	Wet-process phosphoric acid	-	-	6,600b/	0.0088	58	0.166	1,095	0	1,153
2874	Superphosphoric acid	-	-	500b/	0	0	0.007	4	0	4
2874	Normal superphosphate	-	-	390c/	0.0003	0.12	0.470	183	0	183
2874	Triple superphosphate	-	GTSP process	954c/	0.00002	0.02	0.35	334	0	334
		-	ROP process	636	0.0007	0.45	0.11	70	0	70
2874	Ammonium phosphate	-	-	3,550d/ (of P_2O_5)	0.002	15	0.149	1,150	0	1,165
2048	Defluorinated phosphate rock (livestock and poultry feeds)	272 (1977)e/	1.0e/	272	0.33	90	2.2	600	0	690
2048	Animal-feed-grade calcium phosphates	635 (1977)e/	1.0e/	635	0.026	17	2.6	1,651	0	1,668
	B. subtotal					189		5,087	0	5,267
	C. Industrial manufacturing									
2819	Elemental phosphorus	475 (1974)e/	Decrease of 0.7%/yre/	462	0.15	69	0.64	296	0	365
2819	Dry process phosphoric acid	857 (1974) (of P_2O_5)e/	Increase of 0.7%/yre/	883 (of P_2O_5)	0.044	60	0.57	770	0	830
2819	Phosphorus pentoxide	-	-	8e/	0.024	0.2	8.50	68	0	68
2819	Phosphorus trichloride	Capacity (1978) 98.88f/	Assumed 97.5% utilizationg/	96.4	0.05	5	10.8	1,041	2	1,048
2819	Phosphorus oxychloride	Capacity (1978) 83.46f/	Assumed 95% utilizationg/	79.3	0.05	4	4.74	376	0	380
2819	Phosphorus pentasulfide	Capacity (1978) 79.8f/	Assumed 96% utilizationg/	76.6	0.039	3	15.14	1,160	30	1,193
2841	Sodium tripolyphosphate (STPP)	829 (1973)e/	1.0e/	829	0	0	0	0	0	0

TABLE 6-17. (continued)

SIC No.	Industry or activity description	Base data for year ( ) 10^3 MT/Yr	Extrapolation factor or comment	Estimate for 1978 10^3 MT/Yr	Discharges to environment: Discharged wastewater: Emission factor kg P/MT product	Discharged wastewater: MT of phosphorus	Air emissions: Emission factor kg P/MT product	Air emissions: MT of phosphorus	Solid wastes, MT of phosphorus	Total discharge MT of phosphorus
2841	Sodium phosphates (excluding STPP)	339 (1973)e/	Increase of 4%/yre/	353	0.004	1	2.00	706	0	707
2819	Food-grade-calcium phosphates	48 (1976)e/	Increase of 3.5%/yre/	51	0.17	9	2.40	122	0	131
2841	Laundry detergents (phosphorus-based)	-	-	1,860h/	0.029	54	0.007	13	0	67
	Direct acid treatment of metal surfaces (with H_3PO_4)		Consumption rate	34 (of P)e/	0.044	10	0.12	27	0	37
	Phosphorus-based water treatment chemicals	-	Consumption rate	22.7 (of P)h/	-	22,700	0	0	0	22,700
	C. subtotal					22,915		4,579	32	27,526
	D. Municipal sewage treatment effluent	-	-	-		310,000		-	-	310,000
	E. Inadvertant sources									
	Iron manufacture					Data not available	-	3,000	Not applicable	3,000
	Steel manufacture					Data not available	-	280	Not applicable	280
	Cement manufacture					Data not available	-	190	Not applicable	190
	Refuse incineration					Data not available	-	45	Not applicable	45
	Fuel oil combustion					Data not available	-	1,900	Not applicable	1,900
	Coal combustion					Data not available	-	6,000	Not applicable	6,000
	E. subtotal					-		11,415		11,415
	National total, point source					333,326		26,346	32	359,695

a/ Reference 9.

b/ Reference 13.

c/ Reference 14.

d/ Reference 17.

e/ MRI interpretation of data collected from industrial contacts and from Chemical Economics Handbook (published by Stanford Research Institute, 1977).

f/ Reference 27.

g/ Reference 12.

h/ Industrial contacts.

TABLE 6-18. SUMMARY OF ESTIMATED NATIONAL PHOSPHORUS DISCHARGES TO ENVIRONMENT IN 1978

Activity	Phosphorus discharged (metric tons) Wastewater	Air emissions	Solid wastes	Total phosphorus discharged (metric tons)	% of national phosphorus discharge
Nonpoint source discharges for runoff water					
Cropland	1,433,400	Data not available	Data not available	1,433,400	48.9
Pasture and rangeland	985,600	Data not available	Data not available	985,600	33.6
Forest land	84,300	Data not available	Data not available	84,300	2.9
Livestock feed lots	28,700	Data not available	Data not available	28,700	1.0
Urban	18,400	Data not available	Data not available	18,400	0.6
Roadways (rural)	1,000	Data not available	Data not available	1,000	<0.1
Nonpoint inadvertent sources	-	21,410	Data not available	21,410	0.7
Nonpoint subtotal	2,551,400	21,410	None	2,572,810	87.6
Point Source Discharges					
Phosphate rock mining and beneficiation	222	5,265	0	5,487	0.2
Production of phosphate fertilizers and intermediate chemicals	73	2,836	0	2,909	0.1
Production of animal feed	107	2,251	0	2,358	0.1
Production of phosphorus and derived chemicals	151	4,539	32	4,722	0.2

TABLE 6-18. (continued)

Activity	Phosphorus discharged (metric tons) Wastewater	Air emissions	Solid wastes	Total phosphorus discharged (metric tons)	% of national phosphorus discharge
Production of laundry detergents	54	13	0	67	<0.1
Direct acid (H_3PO_4) treatment of metal surfaces	10	27	0	37	<0.1
Phosphorus-based water treatment chemicals	22,700		-	22,700	0.8
Inadvertent sources	-	11,415		11,415	0.4
Municipal sewage treatment effluent	310,000	-	-	310,000	10.6
Point source subtotal	333,317	26,346	32	359,695	12.4
National total	2,884,717	47,756[a]	32	2,932,505[a]	100.0

[a] Rounded to nearest 1,000 metric tons.

	Estimated % of national phosphorus discharge	Type of source point (P) or nonpoint (NP)
1. Cropland runoff	48.9	NP
2. Pasture and rangeland runoff	33.6	NP
3. Municipal sewage treatment effluent	10.6	P
4. Forestland runoff	2.9	NP
5. Inadvertent sources (total for point and nonpoint)	1.1	P + NP
6. Livestock feedlots	1.0	NP
7. Phosphorus-based water treatment chemicals (usage)	0.8	P
8. Urban runoff	0.6	NP
9. Phosphate rock mining and beneficiation	0.2	P
10. Production of phosphorus and derived chemicals	0.2	P
Total	99.9	

Summary of Airborne Phosphorus Pollutants

Table 6-19 shows the estimated annual quantities and percentage distribution of the total phosphorus discharged as air emissions in 1978. A portion of the data was taken from Table 6-17.

Coal combustion is estimated to be the largest single source of phosphorus air emissions (about 23% of national P air emissions) in the United States. This emission occurs as fly ash in stack emissions from combustion. The second largest source (about 20% of the national total P air emissions) is phosphate rock mining and beneficiation activities; phosphorus air emissions from these operations (i.e., mining, handling, drying, calcining, crushing, and grinding) occur as phosphate rock particulate. The estimated third largest source (about 11% of the national total) is iron manufacture; the emission occurs at particulate matter (e.g., ore dust). Fuel oil combustion ranks fourth and represents about 7% of total phosphate air emissions. The manufacture of animal-feed grade calcium phosphates is estimated to account for about 6% of the national air emission of phosphorus. All other estimated source quantities of phosphorus in air emissions are less than 5% of the total national phosphorus air emissions.

Essentially all phosphorus air emissions occur as various particulate forms of phosphorus compounds (e.g., product particulate matter).

At present (1978), there are no air emission control standards for phosphorus compounds in the United States because these air emissions of phosphorus compounds do not create any known problem (Crane, G. B., personal communication, U.S. Environmental Protection Agency, Industrial Studies Branch, Research Triangle Park, North Carolina, December 1978).

TABLE 6-19. ESTIMATED QUANTITIES AND DISTRIBUTION OF TOTAL PHOSPHORUS DISCHARGED AS AIR EMISSIONS IN THE UNITED STATES IN 1978

SIC No.	Industry or activity description	Air emissions MT of phosphorus	% of national phosphorus air emissions	Predominant form(s) of phosphorus in air emissions
	A. Industrial point sources			
1475	Phosphate rock mining and beneficiation	5,265	19.98	Particulate (phosphate rock)
2874	Wet-process phosphoric acid	1,095	4.16	Particulate (rock dust and acid mist)
2874	Superphosphoric acid	4	0.02	Particulate (acid aerosols and mists)
2874	Normal superphosphate	183	0.69	Particulate (phosphate rock and product)
2874	Triple superphosphate: GTSP process	466	1.77	Particulate (phosphate rock and product)
	ROP process	70	0.27	Particulate (phosphate rock and product)
2874	Ammonium phosphate	1,150	4.36	Particulate (product)
2048	Defluorinated phosphate rock (animal feed)	600	2.28	Particulate (phosphate rock and product)
2048	Animal-feed grade calcium phosphates	1,651	6.26	Particulate (product)
2819	Elemental phosphorus	300	1.14	Particulate (phosphate rock and P_2O_5)
2819	Dry process phosphoric acid	770	2.92	Particulate (H_3PO_4)
2819	Phosphorus pentoxide	68	0.26	Particulate (P_2O_5)
2819	Phosphorus trichloride	1,041	3.95	Particulate (P_2O_5 and product)
2819	Phosphorus oxychloride	376	1.43	Particulate (P_2O_5 and product)
2819	Phosphorus pentasulfide	1,160	4.40	Particulate (P_2O_5 and product)
2841	Sodium tripolyphosphate (STPP)	0	0	Not applicable
2841	Sodium phosphates (excluding STPP)	706	2.68	Particulate (product)
2819	Food-grade calcium phosphates	122	0.46	Particulate (product)
2841	Laundry detergents (phosphorus-based)	13	0.05	Particulate (product)
	Direct acid treatment of metals (with H_3PO_4)	27	0.10	Particulate (H_3PO_4)
	Phosphorus-based water treatment chemicals	0	0	Not applicable
	B. Inadvertent point sources			
	Iron manufacture	3,000	11.39	Particulate (ore, etc.)
	Steel manufacture	280	1.06	Particulate
	Cement manufacture	190	0.72	Particulate (fly ash)
	Refuse incineration	45	0.17	Particulate (fly ash)
	Fuel oil combustion	1,900	7.21	Unknown
	Coal combustion	6,000	22.77	Particulate (fly ash)
		26,150	100.00	

REGIONAL QUANTIFICATION OF PHOSPHORUS SOURCES

Most of the data on national assessment of phosphorus losses to environment developed in this report can be applied directly to support the quantification of emissions in regional areas. This relationship exists because most of the point source data apply to representative model production plants (based on 1 MT of product). The emission factors (Table 6-17) can be readily applied to provide estimates of phosphorus discharges for various known production levels. The two key types of data required to prepare these estimates are production or consumption rates and unit emission rates for phosphorus. Also, the information[1/] on nonpoint phosphorus sources is subdivided into data for minor basins, major basins, state and national categories; these subdivisions are amenable to use in studies of specified land areas in the United States.

A discussion of the general methodology suggested for development of regional assessments of environmental phosphorus discharges is presented in this subsection. As an example case to illustrate the application of this methodology, an estimate of the total phosphorus discharge for the state of Florida in 1978 is developed and described. These same procedures could be applied equally well to other land areas of interest, such as various drainage basins, etc., provided that point source data on production and consumption rates are available for industries of concern and nonpoint source loading or land use data are available.

Florida was selected as an example case because many companies operate phosphate rock mining and processing facilities within this state. Processes of interest include the mining and beneficiation of phosphate rock and the production of elemental phosphorus, wet process and dry process phosphoric acid, superphosphoric acid, all types of phosphate fertilizers, defluorinated phosphate rock (animal feed), and feed grade calcium phosphates. The majority of the Florida phosphate rock and phosphate fertilizer processors are located in the central portion of the state (mostly in the adjoining counties of Polk, Hillsborough, Hardee, Manatee, Suwannee, and Hamilton) and comprise a relatively small land area within the state.

These estimates account for all principal sources of phosphorus release.

Quantifications of Nonpoint Sources

The estimated quantities of phosphorus discharged from nonpoint sources to receiving waters in Florida are as shown in Table 5-20.[1/]

Inadvertent Losses from Nonpoint Sources in Florida--

Estimated national data (1978) for phosphorus air emissions were shown in Table 6-1. A brief discussion of estimates for these sources in Florida is provided in the following paragraphs.

TABLE 6-20. ESTIMATED NONPOINT SOURCE DISCHARGES OF TOTAL PHOSPHORUS TO THE ENVIRONMENT IN FLORIDA IN 1978

Source activity or area	Discharges to environment, metric tons of total phosphorus per year	
	Discharged water	Air emissions
A. Runoff discharges		
Cropland	4,650	
Pasture and rangeland	12,930	↑
Forestland	830	
Livestock feedlots	150	Data not available
Urban runoff	510	
Roadway runoff	50	↓
Subtotal for A	19,120	
B. Inadvertent sources		
Windblown soil		55
Fertilizer application (field spreading)	↑	42
Agricultural burning	Data not applicable	32
Forest fires	↓	235
Subtotal for B		364

Sources: Midwest Research Institute data.

Windblown soil--The phosphorus release in these emissions can be estimated on the basis of relative land areas of cropland in Florida and the nation. The acreage of cropland in Florida represents 0.88% of the national total.[1] The national emission is estimated to be 6,300 MT phosphorus (Table 6-1). The estimated total annual quantity of phosphorus from this source in Florida is about 55 MT.

Fertilizer application (field spreading)--The national emission is estimated to be 4,800 MT phosphorus (Table 6-1). From the ratio of Florida cropland area to the national area, the approximate discharge in Florida can be calculated to be approximately 42 MT.

Agricultural burning--On a national basis, the estimated phosphorus emission is 3,600 MT (Table 6-1). Using the ratio of cropland areas (Florida versus national), the emission in Florida can be estimated at 32 MT phosphorus.

Forest fires--The national emission rate is 6,700 MT of phosphorus (Table 6-1). Based on the extent of forested areas in Florida and nationally and the national emission rate (Table 6-1), the state emission can be estimated to be about 235 MT phosphorus.

Quantification of Point Sources in Florida

The estimates of phosphorus released by specified point sources in Florida in 1978 were based primarily on the national emission factor data shown in Table 6-17 and on the relative national and state production or consumption capacities. Information concerning production and consumption rates were obtained from the literature,[27] from contacts with the Florida Chamber of Commerce (Tallahassee), and from contacts with industry representatives. An example of the estimating procedure follows.

Estimated total production of phosphate rock for 1978, as shown in Table 6-17 is 50,348,000 MT. On the basis of relative national and state production capacities,[27] the Florida share of production in 1978 can be estimated at about 76.3% or 38,416,000 MT.

The losses of phosphorus to the environment can be estimated on the basis of the unit emission rate data shown in Table 6-17. The rate of discharge in wastewater is estimated to be 0.005 kg phosphorus per metric ton of phosphate rock product. The total phosphorus discharged is estimated to be 190 MT.

The estimated air emission for Florida, as shown in Table 6-3, is 0.09 kg phosphorus per metric ton product. Thus, the total air emission is calculated to be 3,460 MT phosphorus.

Data provided in the literature[27] show that in 1977 there were no production plants located in Florida for the following products: dry process (furnace) phosphoric acid, sodium phosphates, phosphorus trichloride, phosphorus oxychloride, phosphorus pentasulfide, phosphorus pentoxide, and food grade calcium phosphates. It was assumed that the same situation applies for 1978.

The estimated point source discharges of phosphorus in Florida are tabulated in Table 6-21.

Conclusions for Regional Assessment

The estimated phosphorus discharges for the state of Florida are summarized in Table 6-22. The estimated total phosphorus emission is about 34,100 MT or about 1.2% of the national total.

The aggregate nonpoint source discharges account for 57.1% (~ 19,500 MT phosphorus) of the estimated total phosphorus emissions in Florida. In this category, the runoff water discharges of phosphorus represent about 56% of the total emission for the state and the inadvertent nonpoint sources represent about 1%.

The total discharge from point sources in Florida amounts to about 14,600 MT phosphorus (42.9 of the entire discharge for the state). Major point source emissions are sewage effluent (21.0%), phosphate rock mining and beneficiation (~ 11%), production of animal feed (~ 5%), and production of phosphate fertilizer and intermediate chemicals (4.2%). Inadvertent point source discharges represent approximately 1% of the total for the state.

The Florida distribution of emissions is quite different from that which applies for the nation. For example, in the national assessment, the ratio of total nonpoint to total point emissions was about 7 to 1. In contrast, for Florida the nonpoint source to point source emission ratio was about 1.3 to 1. The cropland runoff emissions of phosphorus are about 49% of the total in the national assessment and only about 14% of the total for the state assessment.

A contrast also exists for the point source discharges. In Florida, sewage effluent accounts for 21% of the total state phosphorus discharge. while on a national basis, the corresponding distribution is only 10.6%. Also, phosphate rock mining and processing and fertilizer and feed production in Florida account for a much higher proportion of total phosphorus emissions than in the case for the national assessment (20% versus about 0.4%).

The 10 largest environmental pollution factors in Florida in terms of total phosphorus discharge are listed below in descending order of importance. The estimated percentages of national phosphorus discharge are shown for comparison.

TABLE 6-21. ESTIMATED POINT SOURCE DISCHARGES OF TOTAL PHOSPHORUS TO THE ENVIRONMENT IN FLORIDA IN 1978

SIC No.	Industry of activity description	Estimated production rate for Florida 1978 (10^3 MT/yr)	Discharges to environment (MT of total P/yr)			
			Discharged wastewater	Air emissions	Solid wastes	Total discharge
1475	A. Phosphate rock mining and beneficiation	18,416	190	3,460	0	3,650
	B. Agricultural consumption of phosphate rock/ manufacturing operations					
2874	Wet process phosphoric acid	3,624	32	602	0	634
2874	Superphosphoric acid	205	0	1	0	1
2874	Normal superphosphate	62	0	29	0	29
2874	Triple superphosphate	1,263	< 1	320	0	320
2874	Ammonium phosphate	1,360 (of P_2O_5)	6	443	0	449
2874	Defluorinated phosphate rock (livestock and poultry feeds)	237	78	522	0	600
2048	Animal feed grade calcium phosphates	196	10	1,030	0	1,040
	Subtotal for B	7,147	126	2,947	0	3,073
	C. Industrial manufacturing					
2819	Elemental phosphorus	41	6	26	0	32
2819	Dry process phosphoric acid	0	0	0	0	0
2819	Phosphorus pentoxide	0	0	0	0	0
2819	Phosphorus trichloride	0	0	0	0	0
2819	Phosphorus oxychloride	0	0	0	0	0
2819	Phosphorus pentasulfide	0	0	0	0	0
2841	Sodium phosphates (including STPP)	0	0	0	0	0
2819	Food grade calcium phosphates	0	0	0	0	0
2841	Phosphorus-based laundry detergents	40	1	< 1	0	1
	Direct acid (H_3PO_4) treatment of metal surfaces	3 (consumption)	1	3	0	4
	Phosphorus-based water treatment chemicals	22.7 (consumption)	227	-	-	227
	Subtotal for C	107	235	29	0	264
	D. Municipal sewage treatment effluent	-	7,177	-	-	7,177
	E. Inadvertent sources					
	Iron manufacture		-	15	-	15
	Steel manufacture		-	3	-	3
	Cement manufacture		-	7	-	7
	Refuse incineration		-	2	-	2
	Fuel oil combustion		-	76	-	76
	Coal combustion		-	300	-	300
	Subtotal for E			403		403
	Total point source		7,728	6,839	0	14,567

TABLE 6-22. SUMMARY OF ESTIMATED PHOSPHORUS DISCHARGES TO ENVIRONMENT IN FLORIDA IN 1978

Activity	Phosphorus discharged (MT)			Total phosphorus discharged (MT)	% of total phosphorus discharge for Florida
	Wastewater	Air emissions	Solid wastes		
Nonpoint source discharges from runoff water					
Cropland	4,650	Not applicable	Not applicable	4,650	13.7
Pasture and rangeland	12,930			12,930	37.9
Forestland	830			830	2.4
Livestock feedlots	150			150	0.4
Urban	510			510	1.5
Roadway	50			50	0.1
Nonpoint inadvertent sources	-	365		365	1.1
Nonpoint subtotal	19,120	365	None	19,485	57.1
Point source discharges					
Phosphate rock mining and beneficiation	190	3,460	0	3,650	10.7
Production of phosphate fertilizers and intermediate chemicals	38	1,396	0	1,433	4.2
Production of animal feed	88	1,552	0	1,640	4.8
Production of phosphorus and desired chemicals	6	26	0	32	0.1
Production of laundry detergents	1	< 1	0	1	< 0.1
Direct acid (H_3PO_4) treatment of metal surfaces	1	3	0	4	< 0.1
Phosphorus-based water treatment chemicals	227	-	-	227	0.7
Inadvertent sources	-	403	-	403	1.2
Municipal sewage treatment effluent	7,177	-	-	7,177	21.0
Point source subtotal	7,772	6,840	0	14,612	42.9
Total for Florida	26,900[a]	7,200[a]	0	34,100[a]	100.0

[a] Rounded to nearest 100 MT.

Florida activity or item	Estimated % of Florida phosphorus discharge	Estimated % of National phosphorus discharge[a]
1. Pasture and rangeland runoff	37.9	33.6
2. Municipal sewage treatment effluent	21.0	10.6
3. Cropland runoff	13.7	48.9
4. Phosphate rock mining and beneficiation	10.7	0.2
5. Animal feeds (feed grade calcium phosphates and defluorinated phosphate rock)	4.8	1.0
6. Phosphate fertilizers and intermediate chemicals	4.2	0.2
7. Forest and rangeland runoff	2.4	2.9
8. Inadvertent sources (total for point and nonpoint)	2.3	1.1
9. Urban runoff	1.5	0.6
10. Phosphorus-based water treatment chemicals	0.7	0.8
Total	99.2	99.9

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[a] Percentage for the type of activity or item on a national basis.

Rational and Ranking Order for Assessing Regional Sources

In the national emission study described earlier, all principal sources of phosphorus in the environment were studied without regard to any assignment of priority to those categories which deserve special attention because of the magnitude and nature of their emissions.

In any regional study, such priority can be assigned if information concerning the potential polluting activities in a region is available. For example, a rationale and accompanying ranking order can be described for Florida.

In the nonpoint source category, emissions should be investigated in the following ranking order (based on results of a national assessment) unless special data are available to support a different ranking.

1. Cropland runoff,

2. Pasture and rangeland runoff,

3. Forestland runoff,

4. Livestock feedlots,

5. Urban runoff, and

6. Roadway runoff.

For point sources, the results of the national emission assessment (Table 6-17) show that the largest emission category is municipal sewage treatment effluent. Thus, this evaluation should rank first in order of importance in the point source studies.

Florida, which has an extremely heavy concentration of phosphate rock production operations, contributes about 78% of the total domestic output of phosphate rock.[27] A review of national assessment data (Table 6-17) shows that phosphate rock processing is a major contributor to phosphorus emissions. Therefore, a study of phosphate rock mining and beneficiation emissions should rank second.

There are large volume operations for animal feed production in Florida.[28] Also, the national assessment results (Table 6-17) show that this category has high phosphorus emission factors. Thus, an investigation of phosphorus discharges from animal feed production should rank third.

There are extensive and large volume production operations for all types of phosphate fertilizer products in the state.[27] Also, the phosphorus emission factors for these operations are fairly high, as shown in Table 6-17. Accordingly, an assessment of emissions from the phosphate fertilizer industry in Florida should rank fourth.

A review of data from the national emission assessment (Table 6-18) indicates that the usage of phosphorus-based water treatment chemicals ranks second to sewage effluent as a principal point emission source. Therefore, an analysis of phosphorus discharges from this activity would rank fifth.

Inadvertent sources are shown in Table 6-18 to rank (in magnitude of phosphorus emissions) just behind water treatment chemicals on a national basis. Therefore, an analysis of inadvertent point sources in Florida should rank sixth.

The national point source discharge data (Table 6-18) show that three industrial categories are all relatively small contributors to phosphorus emissions. These production industries are: (a) phosphorus and derived chemicals; (b) laundry detergents; and (c) direct acid treatment of metal surfaces. The largest contributor (to phosphorus emissions) of these three on the national basis is the first listed category. Therefore, an assessment of the emissions from production of phosphorus and derived chemicals should rank seventh. For the remaining two categories, information impacting on their probable importance in Florida is not readily available. However, since laundry detergents are much more widely utilized than acid for metal treatment, an arbitrary judgment would be to assign a rank of eighth for laundry detergent and ninth for acid treatment operations.

Special Problems in Regional Settings--

There may be a few regions of the United States for which the foregoing methodology for emission assessment is not completely applicable. The emission problems in various regions are unique, require evaluation on a case-by-case basis, and may require some modifications in the suggested quantification procedures. Thus, certain apparently minor phosphorus emission sources may have major significance in certain regional settings but would not be a major contributor on a national scale. Examples would be the domestic production and use of aryl phosphates, treatment of metal surfaces, steel manufacture, etc.

Aryl phosphates are used domestically as fire retardant hydraulic fluids, plasticizers in flexible plastics, and as lubricant additives. The hydraulic fluid usage represents the largest contributor of these esters into the environment. Since reprocessing of waste hydraulic fluid has not been a significant factor until very recently, large quantities of these fluids were directly introduced into the environment.

The production and use of these compounds represent an extremely small percentage of total domestic phosphorus consumption. Because of this small consumption rate, the national and regional assessments do not quantify the phosphorus discharges from these aryl phosphate manufacture and use operations. However, in certain metropolitan areas, extensive utilization of hydraulic equipment which employ and discharge these hydraulic fluids may exist. Thus, the possibility exists in this case that serious phosphorus pollution could occur in certain metropolitan areas due to heavy demand and use of aryl phosphates. Any assessments of phosphorus emissions for very localized areas must be aware of apparently minor sources of this type.

DETERGENT PHOSPHATE BANS IN INDIANA AND NEW YORK

Governmental officials responsible for improving water quality, particularly those in the Great Lakes area, are concerned by the slow rate of progress being made in the improvement of phosphorus control in municipal sewage treatment and are encouraging legislation to implement detergent phosphorus bans in all of the states in the Great Lakes Basin. They state that such action would lower the phosphorus content of municipal effluents until treatment for phosphorus removal is available.29/

The representatives of the detergent industry contend that phosphate compounds are still the most effective and environmentally safe detergent builders. Industry questions the rationale and statistical evidence that have been presented that support detergent phosphorus bans. In addition, the attention being given detergent regulation is claimed to be out of proportion with its actual probable impact on the eutrophication problem.[30-32]

Indiana and New York have become the initial testing ground for the effectiveness of a ban on detergent phosphates. Both states implemented detergent regulations in 1972 which limited the level of total phosphorus in detergent products to 8.7%. The maximum levels were further reduced to 0.5% in 1973.

The following discussion will present the available data for each state. Each state will be examined separately on the basis of: (a) surface water geography, (b) the location and nature of recent water quality problems, and (c) data illustrating the impact of the phosphate ban.

Indiana

Since the implementation of phosphate legislation, Indiana has been more thoroughly monitored than has New York. A discussion of the available data for Indiana follows.

Surface Water Geography--

The primary source of surface water in Indiana is rainfall. Approximately one-third of this precipitation enters the surface drainage system[33] and is eventually discharged into the Ohio River (south) and Lake Michigan (north). Through tributaries, the drainage may also impact on the Mississippi River and Lake Erie.

Indiana's largest watershed is the Wabash River Basin which drains 67% of the state and flows south to the Ohio River. The major tributaries of the Wabash are the east fork and west fork of the White River which run through the central and south central portions of the state. In addition to the Wabash, a number of minor streams empty into the Ohio River along Indiana's southern border.

In the northern portion of the state, the Kankakee River flows west into an Illinois tributary of the Mississippi River. Lake Michigan receives the waters of the Grand Calumet and the Little Calumet Rivers, the Indiana Harbor Canal, Burns Ditch, Trail Creek, and the most northerly of the two St. Joseph rivers. (There are two completely separate streams which bear the name St. Joseph River in Indiana.) To the northeast, the other St. Joseph River joins the St. Mary River and flows eastward through Ohio to Lake Erie via the Maumee River.

Aside from the Lake Michigan shoreline, Indiana does not contain or border on any natural lakes large enough to be included in the USGS list of U.S. lakes covering 26 sq km (> 10 sq miles).[34] Similarly, Indiana has only nine state-owned reservoirs (there are several privately owned enpoundments) and only Monroe has a surface area greater than 26 km (10 sq miles) (J. M. Minster, Personal Communication, Division of Water, Indiana State Department of Natural Resources, Indianapolis, Indiana, November 1978).

Location and Nature of Water Quality Problems--

Water quality problems in Indiana stem primarily from municipal sewage treatment discharges. Wastes from industry and agriculture also aggravate conditions in some areas.[33] In addition to phosphorus, the parameters which command the most interest in municipal effluents are BOD, suspended solids, and fecal coliform. Additional aspects of municipal, industrial, and/or agricultural waste streams that also require regulation include ammonia, nitrate, chemical oxygen demand (COD), phenol, cyanide, sulfate, sulfide, chloride, fluoride, zinc, chromium, and oil and grease.[35]

In recent years, there have been a number of water quality problems along the Lake Michigan shoreline, especially in the Indiana Ship Canal and Inner Harbor Basin (the Indiana Harbor Canal in the Grand Calumet River). This locale must dispose of the wastes of a population approaching one-half million people, as well as the effluents from one of the most concentrated steel and petroleum manufacturing complexes in the nation.[33] The metropolitan areas included are East Chicago, Gary, and Hammond.

In this area, municipal and industrial wastestreams are under the surveillance of the International Joint Commission (IJC). As a result, these wastestreams have been subjected to considerable scrutiny. The following sources of significant phosphorus discharges have been identified to be C. F. Petroleum, Youngstown Sheet and Tube, the sewage treatment plant in East Chicago, the sewage treatment plant in Gary, and the sewage treatment plant in Hammond.[35] The relative size of these discharges is shown in Table 6-23. The data indicate that ammost 90% of the point source phosphorus loading in the Indiana Harbor Canal results from municipal sewage treatment effluents.

No other water quality difficulties in Indiana are of the magnitude of the problems in the Indiana Harbor Canal; however, the Indiana State Board of Health identified eight additional regions where significant stream and river pollution was occurring in 1974 (i.e., generally poor water quality, as indicated by BOD, fecal coliform, nitrate nitrogen, ammonia, and local chemical wastes--as well as the elevated total phosphorus):

- The Little Calumet River from Gary to the Illinois state line.
- Salt Creek below Valparaiso.
- Trail Creek below Michigan City.

TABLE 6-23. PHOSPHORUS LOADING IN THE INDIANA HARBOR CANAL[a]

	kg/day of phosphorus	
	1975	1976
East Chicago		
C. F. Petroleum	b/	82
Youngstown Sheet and Tube	75	b/
East Chicago Sewage Treatment Plant	76	93
Gary		
Gary Sewage Treatment Plant	251	538
Hammond		
Hammond Sewage Treatment Plant	b/	667

a/ Adapted from IJC data.[35,36]

b/ Data was not compiled each year for each site.

- Segments of the Wabash River below Huntington, Logansport, Lafayette, Clinton, and Terre Haute.
- The Mississinewa River below Marion.
- The White River, west fork, from Winchester to below Indianapolis.
- The Ohio River in the Jeffersonville-Clarksville-New Albany area.
- The Maumee River below Fort Wayne.[33]

Each of these areas is located downstream from populated locales and sewage treatment discharges so that large amounts of phosphorus are present in each instance along with a variety of other pollutants.

Statewide, municipal treatment wastes are characterized by high levels of fecal coliform, BOD, COD, and ammonia.

Between 1960 and 1975, 295 fish kills occurred in Indiana; of these, 213 involved greater than 600,000 fish. The majority of these incidents took place in stream or river habitats, and most were the result of elevated BOD's and/or high ammonia levels downstream from municipal discharges. The common phosphorus compounds in sewage treatment wastewaters are not toxic and were not implicated in these problems.[33]

Impact of the Detergent Phosphate Ban--

Two studies have been performed to assess the impact of the Indiana detergent phosphate ban. The first was undertaken by the Indiana State Board of Health, and the second by Purdue University, in cooperation with the FMC Corporation.

Indiana State Board of Health research--In order to quantify the impact of the detergent phosphate ban, the Indiana State Board of Health has compiled pertinent information from data collection procedures that were in effect before and after the new legislation.[33] These procedures included 24-hr surveys of municipal sewage treatment plants and testing carried out at water quality monitoring stations on the major streams. The sewage treatment surveys included 51, 55, 51, and 42 plants in 1971, 1972, 1973, and 1974, respectively. There were also variations in the stream monitoring program during the period of interest. Samples were collected at 58 stations in 1971 and 55 stations in 1972 and 1973 on a biweekly basis. In 1974, 85 stations were sampled monthly. In addition, 10 intensive segment surveys were initiated in 1974 to further characterize changes on major rivers.

These programs produced the following data.[33] The average content (grams per capita per day) of phosphorus in raw sewage was reduced by 56% between 1971 and 1974. During the same period, the average content (grams per capita per day) of phosphorus in the sewage effluents decreased 63%. The difference in these two figures is due to improved treatment facilities at nine of the 42 plants surveyes in 1974. Stream testing showed a decrease from an average concentration of 0.82 mg/liter total phosphorus in 1971 to an average of 0.30 mg/liter total in 1974. Overall, the State Board of Health estimated the total reduction in stream phosphorus loading as a result of the ban to be between 25 and 30%. (This estimate has since been challenged. Due to a possible averaging error, the total reduction in phosphorus loading may have been closer to 20%.[31])

Even though Indiana does not have a substantial quantity of lakes or reservoirs, a cursory examination was also given to this portion of Indiana's waters. The State Board of Health compared their own measurements of total phosphorus concentration in Lake Olin, Mississinewa Reservoir, and Long Lake prior to the ban with those obtained by EPA's National Eutrophication Survey in August of 1973. Lake Olin, which receives a small amount of agricultural runoff but no sewage, showed no change in the total phosphorus concentration during the implementation of the ban. However, both Mississinews Reservoir and Long Lake do receive treated sewage and/or septic tank seepage. As expected, all sampling points in these lakes showed a decrease in phosphorus concentration. A 68% decrease from 1.2 mg/liter total phosphorus to 0.38 mg/liter total phosphorus in a 3-year period (1970 to 1973) in the center of the main basin of Long Lake was the most dramatic reduction noted.33/

The final conclusion drawn by the Indiana State Board of Health was that the phosphate ban had achieved its intended purpose. However, this conclusion was immediately followed by a statement emphasizing the importance of continued improvement in phosphorus removal from sewage treatment discharges and industrial discharges, as well as minimizing nonpoint phosphorus loading.

The publication of a 1976 305(b) report by the Indiana State Board of Health provided no significant additions pertinent to the control of phosphorus.37/

Purdue University, FMC Corporation research--A study similar to the Indiana State Work was carried out during the summer of 1974 by Purdue University and the FMC Corporation.31/ This effort was intended to determine whether or not the detergent phosphate ban had succeeded in making phosphorus a growth limiting nutrient in Indiana's waters. Portions of the Wabash and White River systems were selected for the study due to the large quantity of Indiana's domestic wastewater discharges that they accept. Alternate biweekly water samples were collected at the same sites that had been used previously by the Indiana State Board of Health in the study area.

Chemical analysis provided the concentrations of ortho- and total phosphorus present, as well as the concentrations of other nutrients and trace elements necessary for plant growth. The reported values for total phosphorus concentration ranged from 0.110 to over 2.00 mg/liter.31/ The White River (west fork) contained the highest levels with maximum loading downstream from the municipal discharges of Winchester, Muncie, Anderson, Indianapolis, and Martinsville. As indicated in Table 6-24, a much smaller quantity of treated sewage effluent enters the White River (east fork) or the Wabash River and consequently relatively lower nutrient levels were found in these rivers.

TABLE 6-24. AVERAGE PHOSPHORUS CONCENTRATIONS AND TREATED SEWAGE DISCHARGE RATES IN THE PURDUE/FMC STUDY AREA[a/]

	Avg ortho-phosphorus concentration (mg/ℓ)	Avg total phosphorus concentration (mg/ℓ)	Treated sewage discharge rate (m^3/day x 10^3)
White River, west fork	0.582	0.796	720
Wabash River	0.192	0.423	75.8

a/ Adapted from Etzel, J. E., et al.[31/]

None of the laboratory bioassays showed a positive growth response to phosphorus spiking, indicating the presence of excessive amounts of available phosphorus in the original samples. A lack of any correlation between total phosphorus levels and observed fertilities further suggested the initial phosphorus concentrations in the various samples were all higher than would be required to limit plant growth.

The determination of the presence of surplus phosphorus in the study area involved the following genera of algae: *Cladophora*, *Spirogyra*, *Rhizoclonium*, and *Oedogonium*. A criterion of 0.08% extractable phosphorus or more by weight was used to indicate the presence of surplus phosphorus. As was the case with total phosphorus concentrations in the river water, the quantity of extractable phosphorus in the plant tissue paralleled the amount of upstream treated sewage discharge. The White River (west fork) exhibited the highest values, ranging from 0.076 to 0.170%. The White River (east fork) had the lowest values, ranging from 0.075 to 0.094%. The Wabash samples ranged from 0.099 to 0.137%. According to the Purdue-FMC conclusions, these results suggest that both the White River (west fork) and the Wabash River contain algal biomass with a surplus of phosphorus. The White River (east fork) is a borderline case.

The Purdue-FMC research team concluded that the reduction of stream phosphorus concentrations following the ban was insufficient to be of any biological significance. After the elimination of detergent phosphates, other sources of phosphorus in sewage combined with nonpoint sources to maintain sufficient levels of orthophosphate to create a surplus of this nutrient for plant growth in Indiana's rivers. Phosphorus was not judged to be a growth limiting factor in the study area.

This conclusion was followed by an editorial statement presenting the industry-backed alternative to the detergent phosphate ban, namely, improved sewage treatment including chemical precipitation. Citing extensive use in Sweden, the study suggested that this technology could provide a proven method of phosphorus control.

Discussion--

In a discussion of these two studies, limitations inherent in the data and areas of controversy must be acknowledged. Five areas are presented here.

First, there is a poor data base. Phosphorus levels were not routinely measured in Indiana prior to the 1970's. As a result, no comparison with past averages and normal fluctuations is available. This is further complicated by the predominance of river data in the research. The existing literature which discusses phosphorus loading and eutrophication has been primarily directed toward lake and reservoir habitats. This classification system has not been widely applied to rivers because of the many differences between lake and river ecosystems. These differences are reflected in the current EPA water quality criteria that suggest limiting total phosphorus to 25 μg/liter in lakes, but to 100 μg/liter in freely flowing rivers.[38]

Second, the available data describing the impact of the detergent phosphate ban in Indiana have been developed and interpreted by parties directly involved in the outcome of the analysis. There is a notable absence of research activity by an independent third party.

Third, the ultimate value of the detergent phosphate ban in Indiana, on an overall basis, is undecided. All observers agree that there has been a reduction in stream phosphorus concentrations since 1973. However, the importance of this reduction is dependent on local conditions. In areas where the ~20% decrease in phosphorus loading has been sufficient to initiate a remedy for local water quality problems, the ban can be said to have been worthwhile. In areas where the reduction has not been sufficient to result in water quality improvements, the value of the ban remains questionable. The Purdue-FMC research contends that the latter situation exists along significant portions of the Wabash and White rivers.

Fourth, sufficient time may not have elapsed since the implementation of the phosphorus legislation to allow a good measurement of a nutrient reduction in Indiana's waters. The exchange and recycling of phosphorus among plant and animal tissues, water soluble chemical species, and sediments makes the depletion of excess phosphorus in aquatic ecosystems a gradual process. Remedial action which lowers nutrient loading on a lake or river habitat should not be expected to yield immediate results.

Fifth, the economic impact of phosphate legislation is another source of contention. Those in favor of banning detergent phosphates claim substantial savings due to lowered demand for sewage treatment chemicals and sludge disposal. (Associated reductions in environmental insult via by-products of chemical treatment and sewage sludge incineration are also claimed.)[29] Ban opponents suggest that consumers in ban areas incur substantial dollar losses (~ $5.00 per household per year according to Proctor and Gamble) due to increased rates of detergent usage with nonphosphate products, water softening costs, and repair costs for washing machines engineered to function with phosphate treated washwater.[30]

New York

Compared with Indiana, New York contains and borders on many more lakes and at least an equal number of rivers. This abundance of lake habitat places New York in greater danger of eutrophication problems than that present in Indiana.

Surface Water Geography--

In total, there are around 8,000 lakes and ponds in New York, and 10 of these are large enough to appear on the USGS listing of lakes covering 26 sq km or more (> 10 sq miles). New York has 121 km (75 miles) of shoreline on Lake Erie and greater than 320 km (200 miles) of shoreline on Lake Ontario. After Lakes Ontario and Erie, the next largest lake is Lake Champlain which covers 1,270 sq km (490 sq miles) along the eastern border. Lake Oneida, the largest lake completely within New York's borders, covers 207 sq km (80 sq miles). In addition, New York, has 72 reservoirs, the largest of which is the Sacandaga River Reservoir covering 108 sq km (42 sq miles).[34]

New York contains or borders on numerous small streams and a few larger rivers including:

- The Niagara River, flowing from Lake Erie to Lake Ontario.
- The St. Lawrence River, flowing from Lake Ontario to the Canadian border.
- The Hudson River, flowing south near the eastern border to New York City and the Atlantic Ocean.
- The Delaware River, draining southeastern New York and flowing south to become the Pennsylvania-New Jersey border.
- The Allegheny River, draining western New York and flowing southwest into Pennsylvania.

The Location and Nature of Recent Water Quality Problems--

The most detailed examination of phosphorus related water quality problems in New York is provided by IJC publications.[35,36] Tabulations of nutrient loading from various sources along the Lake Ontario and Lake Erie shorelines are included in these reports. Problem areas are identified and the progress of remedial programs is noted on a yearly basis.

A second source of data illustrating nutrient loading problems in New York is the work of the National Eutrophication Survey. The lake portion of this research effort provides an excellent statewide study of the trophic condition of New York lakes prior to the detergent phosphate ban.

IJC data--The work of the IJC has been oriented toward the identification and solution of all types of water quality problems in the Canadian boundary waters. Past examinations have established the need for improved phosphorus control, particularly in metropolitan areas. The flow of Lakes Superior, Michigan, and Huron into Lake Erie has placed a heavy nutrient load on Lake Erie and, to a lesser extent, also on Lake Ontario. Phosphorus has been singled out as the most easily controlled causitive agent, and remedial programs are under way.[35,36]

The thrust of these IJC programs has centered on improved sewage treatment with an effluent goal of 1.0 mg/liter total phosphorus. The performance of large plants in highly populated areas has been of primary interest. No concentrated effort has been made to quantify the impact of detergent phosphate bans in the affected state and metropolitan regions. Nevertheless, the data collection procedures under way do serve to identify the major point sources of phosphorus discharges (> 95% are municipal sewage treatment facilities).

New York is responsible for only a small fraction of Lake Erie's difficulties, but New York effluents do impact heavily on Lake Ontario. A list of these municipal sources, including all of those discharging > 50 kg/day phosphorus during either 1975 or 1976, is given in Table 6-25. This listing of 16 plants provides over 80% of the total point source phosphorus loading on the Lake Ontario-St. Lawrence River Basin by New York State.

National Eutrophication survey--The National Eutrophication Survey (NES) selected 30 lakes and reservoirs in New York for their 1972 sampling. This coincided with the period immediately following the initial phosphate legislation limiting total detergent phosphorus to 8.7% and precedes the enactment of the phosphate ban. The choice of lakes for the study provided a representative cross-section of natural and man-made lakes. Data describing 23 of the subject lakes and reservoirs were published in 1975 and provide the following information.[40]

TABLE 6-25. MAJOR NEW YORK SEWAGE TREATMENT PLANT DISCHARGES INTO LAKE ONTARIO DURING 1975 AND 1976[a]

	Flow (10^3 m^3/day)		Avg annual P concentration (mg/ℓ)		Total P loading (kg/day)	
	1975	1976	1975	1976	1975	1976
Amherst	29.3	27.4	1.0	4.9	29	134
Amherst S.D. No. 16	28.9	33.4	4.2	3.9	121	130
Auburn	38	42.4	1	2.5	36	106
Brighton (Allen Creek)	21	22.7	-	2.6	59	48
Buffalo	650	661	2.5	2.3	1,650	1,520
Canton	4.6	7.5	-	8.3	13	62.2
Chili	40.3	43.2	3.3	3.4	132	147
Ithaca	23.1	25.3	-	3.4	64	87.3
Lowville	3.2	4.05	1.9	15.8	6	63.9
Monroe County. (N.W. Quad.)	29.3	38.3	3.8	1.6	109	61.2
Niagara Falls	263	201	1.0	-	256	-
North Tonawanda	26.6	28.5	2.5	2.1	56	60
Rochester	262	284	2.0	1.4	522	398
Syracuse	270	296	2.3	1.9	610	565
Tonawanda S.D. No. 2	48.3	50.2	5.4	5.3	259	265
Watertown	23.9	38.5	9.0	1.0	213	38.7

[a] Adapted from Reference 35. Measurements having greater than three significant figures have been rounded to 3.

Of the 23 lakes, 14 were found to be eutrophic. Of these 14, 11 receive sewage treatment wastes either from municipal facilities and/or septic tanks within 91.5 m (100 yards) of the shoreline. The lakes were classified on the basis of physical and chemical characteristics, biological characteristics, nutrient loading, and nutrient export via outlet streams. A summary of pertinent data is presented in Table 6-26.

The Impact of the Detergent Phosphate Ban--

The impact of the detergent phosphate ban in New York remains undecided. No large scale research effort has specifically addressed this question. The best data on nutrient loading in New York are provided by IJC and NES publications, but neither group has attempted to assess the effect of the legislation.

The New York State Department of Environmental Conservation records the phosphorus content of municipal effluents and effluents from all other point sources having a phosphorus limitation in their discharge permit. Recently, this inventory has been computerized which will facilitate examination of the data. To date, no attempt has been made to demonstrate the impact of the phosphate legislation using this information.

Discussion--

Shortcomings present in the New York data are very similar to those described for Indiana in four areas. First, normal averages and fluctuations of phosphorus levels in New York's freshwater habitats prior to the 1970's are not available. Second, the ultimate value of the detergent phosphate ban in New York is undecided. Less documentation showing phosphorus loading reductions due to the ban is available in New York than in Indiana. Third, due to the recycling of phosphorus that is characteristic of aquatic habitats, water quality improvements may not be observed for many years--even if legislation is achieving a significant nutrient reduction. Fourth, the economic impact of the legislation remains a question.

Unlike Indiana, New York does contain a large number of sizable lakes and reservoirs. As shown by Table 6-26, a significant group of these were found to be eutrophic by the NES sampling program prior to the 1973 legislation. The quantity of total phosphorus loading stemming from human sewage was recorded in each case. Follow-up studies on these lakes would provide valuable data in assessing the impact of the detergent phosphate ban.

TABLE 6-26. 1972 NES LAKE AND RESERVOIR DATA FOR NEW YORK STATE[a]

	Trophic condition[b]	Surface area (km^2)	Mean depth (m)	Median total P (mg/ℓ)	Mean chlorophyll a (µg/ℓ)	Limiting nutrient (spring) P or N	Municipal and septic tank P loading (kg/yr)	Nonpoint P loading (kg/yr)	Approximate net lake surface area P loading rate[c] (kg/km^2/yr)
Black L.	E	33.8	-	0.030	13.1	N	0	54,200	373
Cannonsville R.	E	19.4	19.2	0.046	29.9	P	0	82,800	3,020
Cassadaga L.	E	0.8	-	0.026	9.7	P	459	222	501
Chautauqua L.	E	57.2	6.9	0.028	13.3	N	8,420	7,160	Net loss
Conesus L.	E	12.9	8.9	0.020	9.9	N	336	4,590	218
Cross L.	E	8.8	5.5	0.076	19.5	N	59,100	236,000	7,590
Goodyear L.	E	1.5	-	0.026	9.6	P	3,720	18,400	4,040
L. Huntington	E	0.3	-	0.015	6.4	P	5	32	53
Lower St. Regis L.	E	1.9	5.1	0.017	7.9	P	104	658	43.8
Otter L.	E	1.1	-	0.043	13.3	P	0	77	Net loss
Round L.	E	1.3	-	0.076	28.3	N	1,010	5,750	920
Saratoga L.	E	16.3	7.9	0.025	11.8	P	13,300	12,800	853
Swan L.	E	1.3	-	0.042	9.5	N	368	1,020	362
Swinging Bridge R.	E	3.5	13.4	0.057	28.7	P	19,700	4,800	4,140
Garry Falls R.	M	26.1	5.4	0.010	3.1	P	5	18,600	198
Cayuga L.	M	172.0	54.6	0.014	3.2	P	37,400	46,700	254
Long L.	M	16.6	-	0.008	3.5	P	91	7,350	Net loss
Owasco L.	M	26.7	29.3	0.009	8.5	P	-	-	-
Sacandaga R.	M	122.0	7.6	0.009	4.8	P	717	21,200	47.5
Seneca L.	M	175.0	88.7	0.010	6.1	P	48,500	18,500	306
Canadiagua L.	O	43.0	39.0	0.009	4.3	P	2,780	3,260	91.7
Keuka L.	O	47.4	22.6	0.008	5.7	P	744	4,200	54.7
Schroon L.	O	16.7	14.3	0.004	2.1	P	195	6,340	Net loss

[a] Adapted from Reference 40. Measurements having greater than three significant figures have been rounded to 3.

[b] E - eutrophic; M - mesotrophic; and O - oligotrophic.

[c] Total P loading minus total P discharged from outlet streams per surface area per year. Some of the data for phosphorus loading used in calculating these values do not include all of the point sources on the respective shorelines.

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APPENDIX A

CONVERSION FACTORS USED IN PHOSPHORUS TERMINOLOGY*

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* Developed by MRI from data in various technical publications.

To convert from	To	Multiply by
% BPL[a]	% P	0.1997
% BPL	% P_2O_5	0.4576
% P_2O_5	% P	0.4364
% P_2O_5	% BPL	2.1853
% P	% P_2O_5	2.2914
% P	% BPL	5.0073
% P_2O_5	% H_3PO_4	1.381
% P	% H_3PO_4	3.164
% H_3PO_4	% P	0.316
% H_3PO_4	% P_2O_5	0.724

[a] BPL = bone phosphate of lime, i.e., tricalcium phosphage.

APPENDIX B

DESCRIPTIONS OF TYPICAL METHODOLOGY USED TO CALCULATE THE ESTIMATED TOTAL PHOSPHORUS EMISSIONS FROM INDUSTRIAL POINT SOURCES

This appendix provides a description of typical calculation methods used to estimate the total phosphorus emissions from all of the industrial point sources presented in this report.

In all emission estimates discussed in this report, the term phosphorus refers to the total phosphorus content unless otherwise noted. All data on quantification of phosphorus sources are presented in terms of total phosphorus (i.e., kilograms (kg) of total phosphorus per metric ton (MT) of product, or metric tons of total phosphorus per year). One metric ton is equivalent to 1,000 kg or 2,205 lb. Much of the phosphorus data reported in the literature is in terms of phosphorus pentoxide (P_2O_5) content. The percent P_2O_5 can be converted to percent total phosphorus (P) by multiplying by 0.4364. As a matter of convenience in explaining the methodology, a few of the figures and tables shown in the body of this report are also shown in this appendix.

EXAMPLE A: ESTIMATES OF PHOSPHORUS EMISSIONS FROM MINING AND BENEFICIATION OF PHOSPHATE ROCK IN THE EASTERN UNITED STATES

The methodology used in this example is typical of that used for all studies in this report on phosphorus rock mining.

A representative flow diagram describing phosphate mining and processing for eastern states is shown in Figure B-1. A discussion of the phosphorus emission estimates for eastern states is provided in the following paragraphs.

Effluent Wastewater

The treatment of process wastewater streams consists basically of gravity settling through extensive use of ponds.

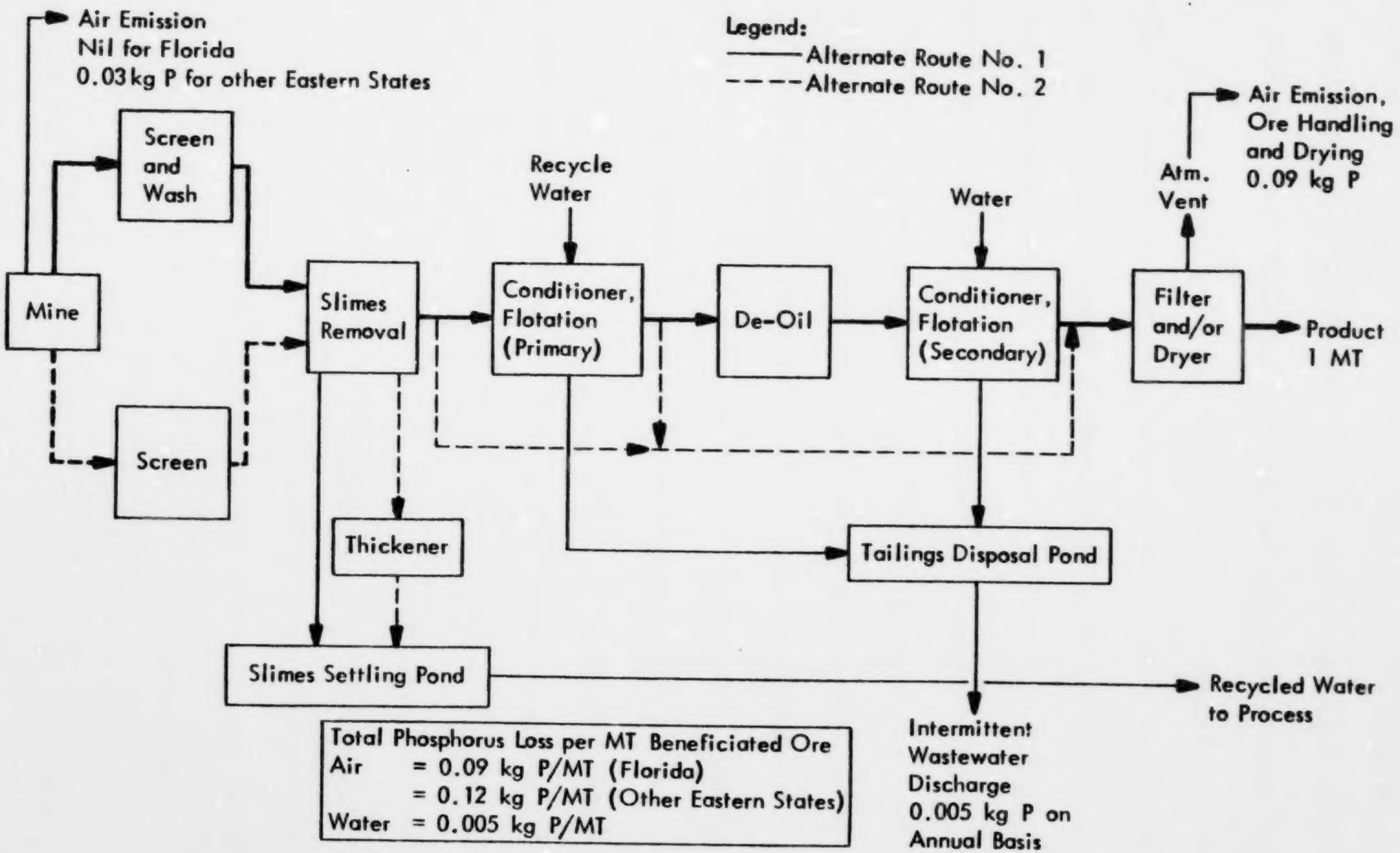
Air Emission
Nil for Florida
0.03 kg P for other Eastern States
Legend:
——— Alternate Route No. 1
- - - - Alternate Route No. 2
Mine
Screen and Wash
Screen
Slimes Removal
Recycle Water
Conditioner, Flotation (Primary)
De-Oil
Water
Conditioner, Flotation (Secondary)
Filter and/or Dryer
Atm. Vent
Air Emission, Ore Handling and Drying 0.09 kg P
Product 1 MT
Thickener
Tailings Disposal Pond
Slimes Settling Pond
Recycled Water to Process
Total Phosphorus Loss per MT Beneficiated Ore
Air = 0.09 kg P/MT (Florida)
= 0.12 kg P/MT (Other Eastern States)
Water = 0.005 kg P/MT
Intermittent Wastewater Discharge 0.005 kg P on Annual Basis

Figure B-1. Flow diagram for phosphate mining and processing--eastern states.

An analysis of 18 eastern facilities for phosphate ore mining (located in Florida, Tennessee, and North Carolina) showed that the average discharge of total phosphorus in the form of phosphate rock amounts to 0.047 kg P/MT of beneficiated ore.

Mr. Elwood E. Martin of the Inorganic Chemical Branch, Effluent Guidelines Division of the U.S. Environmental Protection Agency (EPA) has indicated that approximately one-half of the Florida phosphate fertilizer producers have gypsum pond discharges of wastewater for a total of about 2.5 months out of every year and that, for all practical purposes, this estimate may be extended to the entire United States (Martin, E. E., EPA, Effluent Guidelines Division, Washington, D.C., personal communication, January 1978). On this basis, the phosphorus discharge in plant wastewater can be estimated as follows: 0.047 x 0.5 x 2.5/12, or about 0.005 kg P/MT of beneficiated ore.

Atmospheric Emissions

Air emissions occurring during mining and beneficiation were estimated on the basis of emission data presented in Table B-1.

Mining--

Wet mining operations utilized for Florida land pebble phosphate rock produce essentially no particulate or phorphorus emissions. Therefore, phosphorus air emissions from the activity are considered to be negligible.

During open-pit mining of hard rock phosphate in Tennessee and North Carolina, the ore mining, loading, and hauling result in air emissions of small amounts of phosphate rock particulates. This air emission was estimated as follows based on the assumption that the P_2O_5 content of the particles

TABLE B-1. SOURCES AND ESTIMATES OF PHOSPHORUS-CONTAINING AIR EMISSIONS FOR EASTERN PHOSPHATE ROCK MINING AND BENEFICIATION

Production activity	Uncontrolled particulate emission factor (kg/MT)	% P_2O_5 in emissions	Estimated level of emission control (%)	Total phosphorus emissions--after controls (kg P/MT product)	Comments
Eastern producers					
Mining	0.25	26	0	0.03	Not applicable to Florida wet-mining operations
ore handling	0.5	30	50	0.03	
Drying	7.5	30	94	0.06	
Total				0.12	

emitted to the air is the same as the average P_2O_5 content of the phosphate ore.

The uncontrolled particulate emission factor is 0.25 kg/MT of beneficiated ore, the reported P_2O_5 content in the ore is 26%, and there is no emission control. Thus, the phosphorus emission is estimated to be: 0.25 x 0.26 x 0.4364, or about 0.03 kg P/MT of beneficiated ore.

Beneficiation--

Phosphorus air emissions which occur during the phosphate ore beneficiation process are estimated as follows:

For ore handling, the particulate emission factor is 0.5 kg/MT of beneficiated ore. The P_2O_5 content in the ore is 30% (during beneficiation, some upgrading of the ore occurs by screening operations, etc.). The level of emission control is 50%. The estimated emission is equal to: 0.5 x 0.3 x 0.5 x 0.4364, or about 0.03 kg P/MT of beneficiated ore product.

For drying of the phosphate rock concentrate, the reported uncontrolled emission is 7.5 kg of particulate per metric ton of beneficiated ore, the particulate contains 30% P_2O_5, and the emission control is 94%. Therefore, the estimated emission is equal to: 7.5 x 0.3 x (100% - 94%) x 0.4364, or about 0.06 kg P/MT of beneficiated ore.

Summary of Phosphorus Losses to the Environment

For estimating purposes, it was assumed that the ore mining and production patterns for 1978 were the same as those reported for 1975: Florida, 78%; North Carolina, 5%; Tennessee, 5%; and western states, 12%. Thus, the eastern operations accounted for 88% of total beneficiated ore production.

A summary of phosphorus emissions from eastern phosphate mining and beneficiation (basis 1 MT of beneficiated ore, see Table B-1) follows:

Total atmospheric losses for Florida

$= 0.03 + 0.06$

$= 0.09$ kg P/MT

Total atmospheric losses for all other eastern states

$= 0.03 + 0.03 + 0.06$

$= 0.12$ kg P/MT

The weighted average atmospheric loss for all eastern states is:

$$= \left(\frac{0.78}{0.88} \times 0.09\right) + \left(\frac{0.10}{0.88} \times 0.12\right)$$

$= 0.080 + 0.014$

$= 0.094$ kg P/MT

Total wastewater losses for all eastern states

$= 0.005$ kg P/MT

National Emissions for Mining and Beneficiation of Phosphate Rock

In 1976, the total U.S. marketable production of beneficiated phosphate rock was reported to be 44,452,000 MT (Table 6-17, p. 57). Based on information in the literature, production is estimated to increase to 56,245,200 MT in 1980. Assuming a uniform growth rate from 1976 to 1980, the production level for 1978 can be estimated to be 50,348,000 MT of beneficiated phosphate rock.

The phosphorus emission loss in wastewater for all eastern operations can be estimated as: 0.88 x 50,348,000 x 0.005/1,000, or about 220 MT phosphorus.

There are no significant air emissions from Florida wet mining operations. Open-jet mining in North Carolina and Tennessee does account for phosphorus emissions. Also, ore handling and drying operations for all eastern ores contribute to phosphorus air emissions. The weighted air emissions factor for all eastern operations is 0.094 kg P/MT beneficiated ore. The estimated overall phosphorus air emission for all eastern states is: $44,306 \times 0.094 \simeq 4,165$ MT phosphorus.

EXAMPLE B: ESTIMATES OF PHOSPHORUS EMISSIONS FROM PRODUCTION OF NORMAL SUPERPHOSPHATE FERTILIZER

The methodology described in the following example for normal superphosphate (NSP) fertilizer is representative of the estimating procedures used for the other phosphate fertilizer and phosphate animal feed products discussed in this report. The technologies which are represented by this example include wet-process phosphoric acid production, superphosphoric acid production, triple superphosphate, ammonium phosphates, animal food calcium phosphate, and defluorinated phosphate rock.

A representative process flow diagram for production of NSP is shown in Figure B-2.

Material Balance Data

The weight ratio of phosphate rock to NSP product is 0.605 to 1, when the feed material contains 34.3% P_2O_5 (or 14.98% phosphorus). Thus, 1 MT of product is equivalent to 0.605 MT of phosphate rock. The average P_2O_5 content

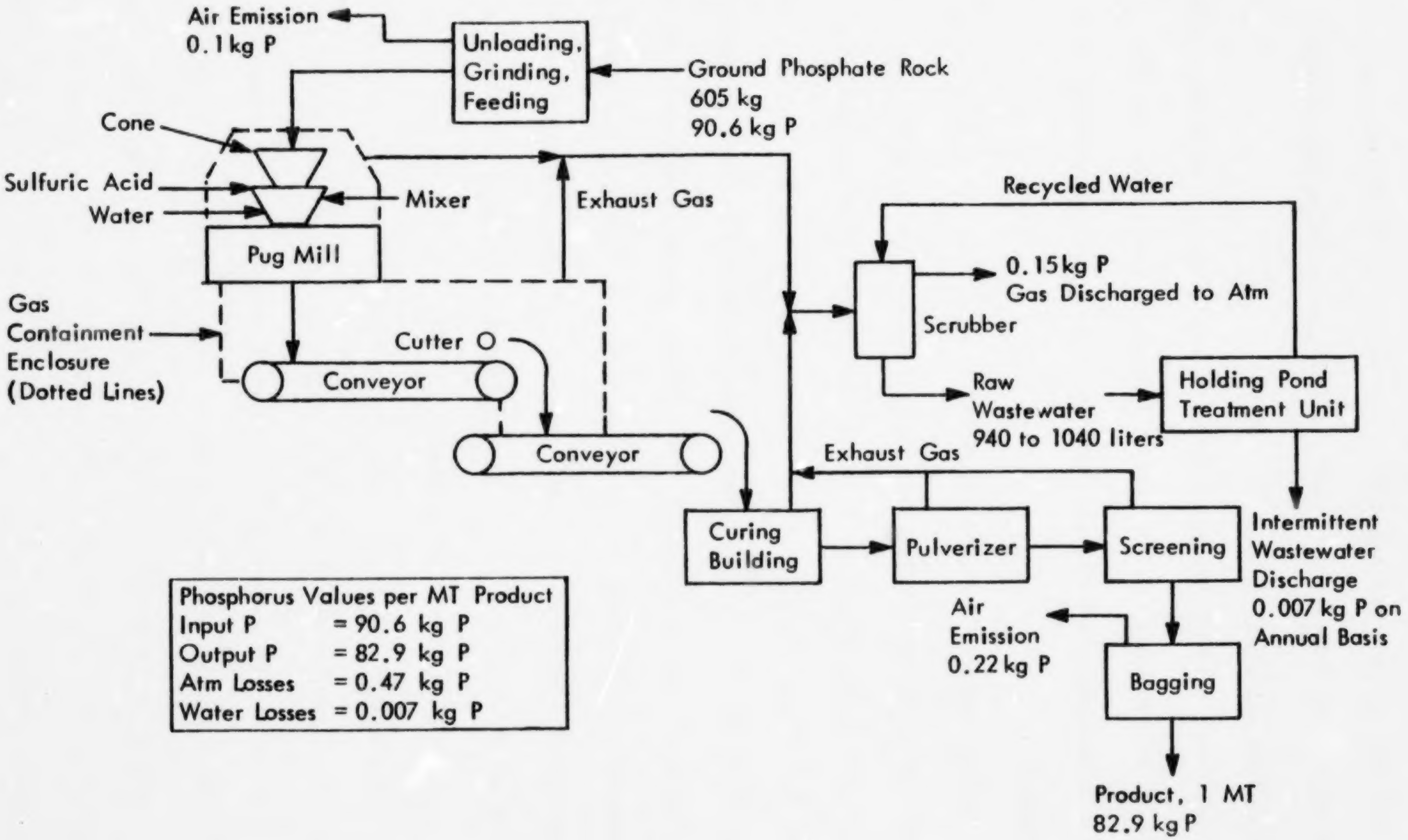
Air Emission
0.1 kg P
Unloading, Grinding, Feeding
Ground Phosphate Rock
605 kg
90.6 kg P
Cone
Sulfuric Acid
Water
Mixer
Pug Mill
Exhaust Gas
Recycled Water
0.15 kg P
Gas Discharged to Atm
Scrubber
Gas Containment Enclosure (Dotted Lines)
Cutter
Conveyor
Conveyor
Raw Wastewater
940 to 1040 liters
Holding Pond Treatment Unit
Exhaust Gas
Curing Building
Pulverizer
Screening
Intermittent Wastewater Discharge
0.007 kg P on Annual Basis
Air Emission
0.22 kg P
Bagging
Product, 1 MT
82.9 kg P
Phosphorus Values per MT Product
Input P = 90.6 kg P
Output P = 82.9 kg P
Atm Losses = 0.47 kg P
Water Losses = 0.007 kg P

Figure B-2. Flow diagram for production of normal superphosphate.

in the NSP product was assumed to be 19% (or 8.29% phosphorus). One metric ton of product contains: 1,000 x 0.0829, or 82.9 kg phosphorus.

Wastewater Effluent

Current information on wastewater containment practices indicates that only 4% of the domestic NSP plants discharge wastewater and that practically all discharging plants treat their wastewater to remove most of the contained phosphorus.

It was assumed in this report that a holding and treatment pond is provided for each fertilizer plant operation and that wastewater is impounded and reciruclated in the plant. Also, it was assumed that the phosphorus content in treated effluent from NSP plants corresponds to the EPA effluent limitation guidelines for best practicable control technology currently available (i.e., a maximum average discharge for 10 or more consecutive days of 35 mg of total phosphorus per liter of wastewater). It was further assumed that for those plants which discharge effluent, the total discharge period each year would be 2.5 months (Martin, E. E., EPA, Effluent Guidelines Division, Washington, D.C., personal communication, January 1978).

The range of discharge rates of contaminated wastewater from the process is 940 to 1,040 liters/MT of NSP product. An average flow rate of 990 liters/MT is assumed. The estimated discharge of phosphorus in wastewater to the environment is calculated as follows: $990 \times 0.035/1{,}000 \simeq 0.035$ kg P/MT of NSP product. For a 2.5 month period of discharge each year, the annual phosphorus release in wastewater would be equal to: $2.5/12 \times 0.035$, or 0.007 kg P/MT of NSP product.

Atmospheric Emissions

The air emission points in NSP production are the ore grinding operation, phosphate rock unloading and feeding, the mixer, the curing building, product pulverizing, and bagging losses. Sources and estimates of phosphorus-containing air emissions for NSP production are shown in Table B-2. The estimating procedures used are described below.

Grinding of Phosphate Rock--

The uncontrolled particulate emission is reported to be 3 kg/MT of NSP product. Also, the particulate contains 34% P_2O_5, and the level of emission control is 80%. The emission is calculated to be: $3 \times 0.34 \times 0.4364 \times (100\% - 80\%) \cong 0.09$ kg P/MT of NSP.

Material Handling--

The average controlled emission factor for unloading phosphate rock is 0.28 g of particulate per kilogram of P_2O_5 contained in product (NSP). The phosphate rock contains 34% P_2O_5, and the product contains 19% P_2O_5. The unloading emission is calculated as: $0.28/1{,}000 \times (1{,}000 \times 0.19) \times 0.34 \times 0.4364 \cong 0.008$ kg P/MT of NSP.

For phosphate rock feeding, the controlled emission is reported to be 0.055 g of particulate per kilogram of P_2O_5 in NSP. The feeding emission is calculated as: $0.055/1{,}000 \times (1{,}000 \times 0.19) \times 0.34 \times 0.4364 = 0.0016$ kg P/MT of NSP.

Mixer and Den--

A reported controlled emission factor for this source is 0.26 g of particulate per kilogram of P_2O_5 in NSP product. Thus, the phosphorus emission

TABLE B-2. SOURCES AND ESTIMATES OF PHOSPHORUS-CONTAINING AIR EMISSIONS FOR NORMAL SUPERPHOSPHATE PRODUCTION

Production activity	Uncontrolled particulate emission factor (kg/MT product)	Controlled emission factor (g of particulate per kg P_2O_5 in product)	Estimated level of emission control (%)	% P_2O_5 in emissions	Total P emissions after controls (kg P/MT product)
Grinding phosphate rock	3	NA	80	34	0.090
Material handling:					
Phosphate rock unloading	NA	0.28	NA	34	0.008
Phosphate rock feeding	NA	0.055	NA	34	0.002
Mixer and den	NA	0.26	NA	19	0.004
Curing building	NA	3.6	NA	19	0.057
Product grinding	0.25	NA	80	a/	0.02
Product screening	1	NA	85	a/	0.07
Product bagging or bulk loading	0.5b/	NA	b/	a/	0.22
Total					0.47

a/ Emission factor includes % P_2O_5.

b/ Emission factor after control.

NA = Not available.

is estimated as: 0.26/1,000 x (1,000 x 0.19) x 0.19 x 0.4364 = 0.004 kg P/MT of NSP.

Curing Building--

The controlled emission factor is 3.6 g of particulate per kilogram of P_2O_5 in product. The phosphorus emission is estimated as: 3.6/1,000 x (1,000 x 0.19) x 0.19 x 0.4364 = 0.057 kg P/MT of NSP.

Product Grinding--

The uncontrolled particulate emission factor is 0.25 kg/MT of NSP, and the level of emission control is 80%. On this basis, the emission is estimated as: 0.25 x (100% - 80%) x 0.4364 = 0.02 kg P/MT of NSP.

Product Screening--

The estimated uncontrolled emission factor is 1 kg of particulate per metric ton of NSP, and the level of emission control is 85%. Thus, the emission is estimated as: 1 x (100% - 85%) x 0.4364 = 0.07 kg P/MT of NSP.

Product Bagging or Bulk Loading--

The reported controlled emission factor is 0.5 kg P_2O_5/MT of NSP. The emission is estimated as: 0.5 x 0.4364 = 0.22 kg P/MT of NSP.

Summary of Phosphorus Losses to the Environment

A phosphorus mass balance showing values which apply for 1 MT of product NSP follows:

Input	Phosphorus (kg)	Total phosphorus losses (kg)
Phosphorus	90.6 (605 kg x 14.98% P)	-
Outputs		
Product NSP	82.9 (1,000 kg x 8.29% P)	-
Wastewater discharge	0.007	0.007
Atmospheric losses:		0.47
From unloading, grinding, and feeding ore	0.1	
From wet scrubber	0.15	
From product bagging	0.22	
Total water effluent and atmospheric losses		0.477

National Emission for NSP Production

As shown in Table 6-17, the estimated NSP manufacturing rate for the United States in 1978 is 390,000 MT.

About 4% of the domestic NSP producers discharge wastewater. The rate of phosphorus discharge in plant wastewater has been estimated to be 0.007 kg P/MT of NSP product. On this basis, the estimated national emission in 1978 is: 0.04 x 0.007/1,000 x 390,000 = 0.11 MT.

Based on the data shown in Table B-2, the estimated total phosphorus air emissions during manufacture of NSP amount to 0.47 kg P/MT of product. Thus, the national air emission for 1978 for NSP production is estimated as: 0.47/1,000 x 390,000 = 183 MT of phosphorus.

EXAMPLE C: ESTIMATES OF PHOSPHORUS EMISSIONS FROM PRODUCTION OF PHOSPHORUS TRICHLORIDE

The methodology used in this example is also representative of that used for each of the following production activities.

- Production of elemental phosphorus
- Production of phosphoric acid by the dry process
- Phosphorus pentoxide production
- Phosphorus oxychloride production
- Phosphorus pentasulfide production
- Sodium tripolyphosphate production
- Production of sodium phosphates
- Production of food grade calcium phosphates
- Production of laundry detergents
- Metal surface treatment

A representative process flow diagram for production of phosphorus trichloride is shown in Figure B-3.

Material Balance Data

Published information shows that a typical material balance (basis 1 MT of phosphorus trichloride product) for the process is as follows:

Raw materials	Kilograms	Product	Kilograms
Phosphorus	238	PCl_3	1,000
Chlorine	815		

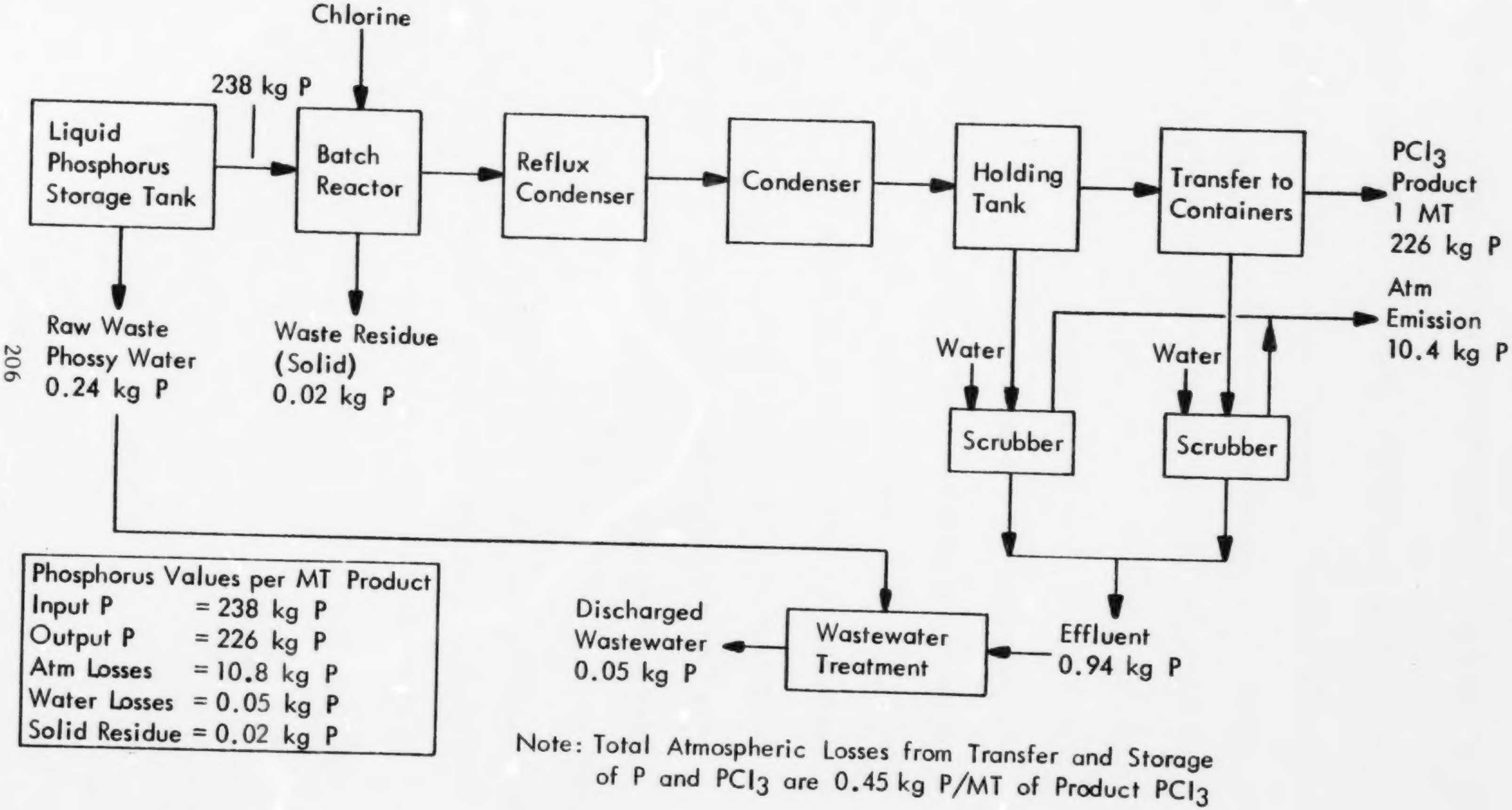
Chlorine
238 kg P
Liquid Phosphorus Storage Tank
Batch Reactor
Reflux Condenser
Condenser
Holding Tank
Transfer to Containers
PCl3 Product
1 MT
226 kg P
Atm Emission
10.4 kg P
Raw Waste Phossy Water
0.24 kg P
Waste Residue (Solid)
0.02 kg P
Water
Water
Scrubber
Scrubber
Phosphorus Values per MT Product
Input P = 238 kg P
Output P = 226 kg P
Atm Losses = 10.8 kg P
Water Losses = 0.05 kg P
Solid Residue = 0.02 kg P
Discharged Wastewater
0.05 kg P
Wastewater Treatment
Effluent
0.94 kg P
Note: Total Atmospheric Losses from Transfer and Storage of P and PCl3 are 0.45 kg P/MT of Product PCl3

Figure B-3. Flow diagram for production of phosphorus trichloride.

The phosphorus content in the pure product is 22.55%; therefore, the estimated amount of phosphorus contained in 1 MT (1,000 kg) of PCl_3 is 225.5 kg.

Wastewater Effluent

Raw wastes are generated by phosphorus storage and transfer, wet-scrubbing of gases, vessel cleaning, and leaks and spills.

Wastewater discharged from the scrubber for distillation tail gases is reported to contain 2.5 kg of H_3PO_3 per metric ton of product. The estimated phosphorus content is calculated as: $2.5 \times 30.975/82 = 0.94$ kg P/MT of PCl_3.

One kilogram of phosphorus is reported to be discharged in the phossy water waste for each metric ton of phosphorus consumed in the production process. Production of 1 MT of phosphorus trichloride requires 0.238 MT of phosphorus; therefore, the total phosphorus discharged in phossy water is 0.238 kg/MT of PCl_3. Combining this figure with the 0.94 kg stated above gives a total phosphorus content in wastewater of 1.18 kg P/MT of PCl_3 product.

It is assumed that the wastewater is treated in pollution control equipment so that the phosphorus contained in treated discharged wastewater is 0.05 kg/MT of PCl_3 product. This value is specified in the EPA effluent limitation guidelines for best practicable technology currently available.

Atmospheric Emissions

The transfer and storage of phosphorus and phosphorus trichloride account for the equivalent loss of 2 kg of PCl_3 per metric ton of PCl_3 product. Thus, the corresponding emission of phosphorus can be calculated as: 30.975/137.35 x 2 = 0.45 kg P/MT of PCl_3.

The quantity of phosphorus discharged from scrubber vents can be calculated, by difference, from a material balance (inputs = outputs plus losses), using data shown on Figure B-3, as follows: 238 - 226 + 0.24 +0.02 + 0.94 + 0.45 + scrubber vent emission. Scrubber vent emission = 10.35 kg P/MT of PCl_3.

Thus, the estimated total atmospheric loss is: 10.35 + 0.45 = 10.8 kg P/MT of PCl_3.

Solid Waste Residue

Solid waste, which is removed periodically from the reactor-still, reportedly contains 0.1 kg of PCl_3 per metric ton of product. The quantity of phosphorus contained in this waste is calculated as follows: 0.1 x 30.975/137.35 = 0.02 kg P/MT of product PCl_3.

Summary of Phosphorus Losses to the Environment

A phosphorus mass balance showing values which apply for 1 MT of product phosphorus trichloride follows.

Input	Phosphorus (kg)
Phosphorus	238
Outputs	
Product	226
Accounted for phosphorus losses	
Total wastewater losses	0.05
Total atmospheric losses	10.8
Total solid waste residue	0.02
Total	10.87
Unaccounted for phosphorus	1.13

National Emission for PCl_3 Production

As shown in Table 6-17, the estimated PCl_3 manufacturing rate for the United States in 1978 is 96,400 MT. On this basis, the national emissions of phosphorus can be estimated as follows:

For discharged wastewater, the estimated phosphorus emissions are:

$0.05/1,000 \times 96,400 = 4.8$, or approximately 5 MT.

For air emissions, the calculated phosphorus losses are:

$10.8/1,000 \times 96,400 = 1,041$ MT.

For solid wastes, the estimated phosphorus losses are:

$0.02/1,000 \times 96,400 = 1.9$, or approximately 2 MT.

EXAMPLE D: ESTIMATES OF PHOSPHORUS LOADING IN TREATED EFFLUENT FROM MUNICIPAL SEWAGE TREATMENT PLANTS

The general procedures used for calculation of the phosphorus loads in treated effluent from municipal sewage treatment plants are presented in the body of this report. The following Table (Table B-3) shows the types of data used in these estimates, and provides a state-by-state evaluation of the phosphorus loads. These data were developed from information provided in the 1976 Needs Survey.* These tabulated data serve to clarify the methodology used in determining the regional phosphorus loads shown in this report.

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* Municipal Construction Division of U.S. Environmental Protection Agency (EPA 430/9-76-010, 430/9-76-011, and 430/9-76-012). Cost Estimates for Construction of Publicly Owned Wastewater Treatment Facilities--1976 Needs Survey.

Table B-3. ESTIMATED 1978 PHOSPHORUS LOAD FROM PUBLICLY OWNED MUNICIPAL TREATMENT PLANTS

State	Population (x 1,000)	% Pri.	% Sec.	% Ter.	Flow (x 10^6 liters/day)	% P removal	P in treated effluent		
							P, domestic and household (MT/year)	P, commercial and industrial (MT/year)	P total (MT/year)
Northeast:									
ME	521	5.9	21.0	7.6	379	1.1	570	643	1,213
NH	407	14.1	14.6	6.8	231	2.7	451	346	797
VT	287	17.8	26.9	3.8	301	7.9	308	1,366	1,674
MA	1,662	4.9	10.7	6.0	1,205	3.9	1,716	1,921	3,637
RI	498	6.4	12.3	8.9	408	0.2	539	769	1,308
CN	2,288	10.1	50.1	4.3	1,644	2.2	2,565	2,818	5,383
Subtotal							6,149	7,863	14,012
Middle Atlantic:									
NY	17,690	20.5	22.2	25.8	9,986	4.5	18,214	10,903	29,117
NY	7,147	17.0	13.5	52.9	4,136	1.5	7,328	4,331	11,659
PA	10,641	23.4	18.7	21.6	7,331	4.0	11,264	11,359	22,623
Subtotal							36,806	26,593	63,399
South Atlantic:									
DE	585	2.2	1.1	13.6	368	0.2	526	425	951
MD	3,200	1.3	18.7	28.4	1,609	14.0	2,733	1,089	3,822
DC	1,965	0.0	0.0	104.7	1,113	20.0	1,379	839	2,218
VA	3,649	17.4	10.9	25.0	1,717	5.0	3,661	1,075	4,736
WV	955	15.5	22.2	12.8	300	0.0	1,062	494	1,556
NC	3,066	3.9	14.3	26.1	2,308	1.8	3,005	2,680	5,685
SC	1,925	7.4	22.9	18.0	1,515	1.9	2,008	2,652	4,660
GA	3,030	11.8	26.8	20.3	2,231	3.2	3,781	3,216	6,997
FL	6,524	3.5	10.6	40.2	2,968	7.3	5,773	1,404	7,177
Subtotal							23,928	13,874	37,802
East North Central:									
OH	9,544	17.4	10.9	43.8	6,246	15.8	8,113	7,499	15,612
IN	4,297	9.0	15.1	23.8	3,069	6.0	4,017	4,356	8,373
IL	11,101	4.6	15.4	36.0	9,352	1.2	10,773	16,164	26,937
MI	7,740	8.4	16.2	19.4	6,523	17.5	6,742	10,004	16,746
WI	3,471	3.8	29.4	21.4	2,514	13.4	3,206	3,581	6,787
Subtotal							32,851	41,604	74,455
East South Central:									
KY	1,639	6.6	17.0	12.2	1,066	9.3	1,599	1,402	3,001
TN	2,634	7.5	9.8	17.0	2,003	0.1	2,750	3,344	6,094
AL	2,380	3.1	25.5	26.3	1,599	0.0	2,438	2,308	4,746
MS	1,263	17.4	21.6	12.7	1,329	0.1	1,533	3,661	5,194
Subtotal							8,320	10,715	19,035
West North Central:									
MN	3,615	4.2	13.7	23.5	2,396	0.1	3,521	2,276	5,797
IA	2,461	29.7	17.8	19.9	1,444	0.0	2,745	1,341	4,086
MO	4,702	40.4	23.2	3.9	2,489	0.0	5,510	2,719	8,229
ND	427	9.8	20.6	23.0	172	0.0	451	37	488
SD	408	15.4	15.5	21.6	191	0.0	436	125	561
NE	1,180	16.6	24.2	32.0	371	0.0	1,443	761	2,204
KS	1,395	40.8	21.1	2.5	348	0.0	2,770	386	3,156
Subtotal							16,876	7,644	24,520

(continued)

Table 8-3. (continued)

State	Population (x 1,000)	% Pri.	% Sec.	% Ter.	Flow (x 10⁶ liters/day)	% P removal	P in treated effluent: P, domestic and household (MT/year)	P in treated effluent: P, commercial and industrial (MT/year)	P in treated effluent: P total (MT/year)
West South Central:									
AR	1,209	24.2	19.1	11.0	684	0.0	1,379	831	2,210
LA	2,784	23.4	32.2	13.6	1,190	0.0	3,149	518	3,667
OK	2,171	20.9	24.3	21.3	1,015	0.8	2,359	570	2,929
TX	10,867	1.5	3.2	69.0	5,396	0.4	9,779	4,282	14,061
Subtotal							16,666	6,201	22,867
Mountains:									
MT	554	25.9	16.9	2.0	385	0.0	662	677	1,339
ID	401	17.4	23.1	4.0	313	2.2	956	393	1,349
WY	335	44.0	21.9	5.0	159	0.0	400	123	523
CO	2,340	3.8	50.0	14.3	1,613	0.1	2,783	2,303	5,086
NM	965	5.0	55.4	1.9	375	0.6	987	171	1,158
AZ	1,991	4.6	11.6	16.2	731	0.0	2,142	0	2,142
UT	1,137	1.2	33.2	38.2	329	0.0	1,145	1,297	2,442
NV	738	5.4	6.0	73.3	445	11.8	338	934	1,272
Subtotal							[illegible]	5,898	14,871
Pacific:									
WA	2,677	29.0	12.5	11.5	1,915	1.4	3,430	3,297	6,727
OR	2,040	0.1	30.8	34.4	[illegible]	0.0	2,051	2,371	4,422
CA	20,388	32.2	10.1	22.2	9,353	1.2	21,734	5,345	27,249
AK	235	29.8	14.8	2.0	126	0.9	281	142	423
HI	427	5.4	11.9	10.4	227	[illegible]	456	224	680
Subtotal							[illegible]	11,379	[illegible]
Total United States (rounded to nearest 1,000)							177,000	133,000	310,000